THERMAL AND CATALYTIC CRACKING OF ARABIAN LIGHT CRUDE OIL TO LIGHT OLEFINS

BY

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This work is dedicated to my beloved family

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LIST OF ABBREVIATIONS

FCC	:	Fluid Catalytic Cracking
AL	:	Arabian Light
ASL	:	Arabian Super Light
AXL	:	Arabian Extra Light
MMT	:	Million Metric tone
PDH	:	Propane Dehydrogenation
MTO	:	Methanol-to-Olefins
MTP	:	Methanol-to-Propylene
CTO	:	Coal-to-Olefins
LPG	:	Liquefied Petroleum Gas
ASTM	:	American Society for Testing Materials
USY	:	Ultra Stable Y zeolite
VGO	:	Vacuum Gas Oil
AR	:	Atmospheric Residue
VR	:	Vacuum Residue
LCO	:	Light Cycle Oil

HCO	:	Heavy Cycle Oil
TAME	:	Tertiary Amyl Methyl Ether
MTBE	:	Methyl Tertiary Butyl Ether
C/O	:	Catalyst to Oil ratio
CMR	:	Cracking Mechanism Ratio
HTC	:	Hydrogen Transfer Coefficient
ACE	:	Advanced Cracking Evaluation

ABSTRACT

Full Name : [Akram Abdulhakeem Al-Absi]

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Thermal and catalytic cracking of three kinds of light crude oils namely Super Light (ASL), Extra Light (AXL) and Arabian Light (AL), which have API gravities of 51°, 39°, and 34°, respectively, have been investigated in a fixed bed Micro-Activity Test (MAT) unit. For catalytic cracking, two catalysts were used, a steamed commercial MFI catalyst (M-cat) and an equilibrium FCC catalyst (E-cat). For thermal and catalytic cracking of AL crude oil, results were compared at the same conversion 34% at 650 °C. For both, as temperature increased yields of light olefins, LPG, dry gas, and coke increased associated with a consistent decrease in heavy ends (LCO and HCO). The superiority of catalytic cracking over thermal cracking for propylene yield was interpreted in terms of mechanisms of free radicals and carbenium ions. Thermal cracking gave a higher yield of ethylene. At high temperature (650 °C) and catalyst to oil ratio (C/O) of 4, light olefins yield decreased in order M-cat (32.7 wt.%,) > E-cat (30.3 wt.%) > thermal cracking (22.8 wt.%). Highest yields of ethylene and propylene (10.9 wt.% and 15.7 wt.%), achieved over M-cat at 650 °C, are attributed to shape selectivity and higher acidity. Naphtha yield for E-cat was much higher than for M-cat: for instance, at 550 °C it was 48.3 wt.% for E-cat and 24.4 wt.% for M-cat. This was attributed to diffusion limitations for M-cat. Effect of C/O ratio on conversion and yields was also inspected, and showed that after C/O of 4 further increases

had only a minor effect. In addition, effect of mixing E-cat and M-cat at different percentages was evaluated and showed an optimum point at 30% M-cat, with corresponding yields of ethylene and propylene of 9.9 wt.% and 19.2 wt.%, respectively. Lastly, thermal and catalytic crackability of the three crudes were also investigated. For thermal cracking case at 650 ºC, yields of corresponding ethylene and propylene increased in order: ASL (6.1 and 6.8 wt.%) < AXL (6.5 and 6.9 wt.%) < AL (7.6 and 8.6 wt.%) crude oils. For catalytic cracking over (30 % M-cat and 70% E-cat), highest yield of ethylene and propylene for ASL, AXL, and AL were 32.2, 31.2, and 29.9 wt.% respectively, were achieved at 650 ºC and a C/O ratio of 6.

ملخص الرسالة

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التكسير الحراري والحفزي لثلاثة أنواع من النفط العربي وهي: ASL العربي شديد الخفة و AXL العربي الخفيف جدا و AL العربي الخفيف التي تمتاز بكثافة 51 و 39 و 34 API° على التوالي، تمت دراسته عبر وحده تكسير مصغرة. تم استخدام نوعين من المحفزات للتكسير الحفزي هما: حفاز متعادل (E-cat) و حفاز MFI تم معالجته بالبخار.

بالنسبة للتكسير الحراري والحفزي للنفط العربي الخفيف تمت مقارنتهما عند تحويل 34% ودرجة حرارة 650 درجة مئوية ثابتتين. لكلا التكسيران كلما زادت درجة الحرارة زادت الإنتاجية لكل من الألكينات الخفيفة وغاز النفط المسال و الغاز الجاف والفحم وهذه الزيادة قابلها نقصان في السوائل ذات درجات الغليان المرتفعة LCO و HCO. التفوق الملاحظ للتكسير الحفزي مقارنة بالحراري في إنتاجية البروبلين تم عزوه الى طرق الجذور الحرة وأيونات الكاربينيوم. عند درجة حرارة 650° ونسبة عامل حفاز الى نفط 4 إنتاجية الألكينات الخفيفة تناقصت بالترتيب التالي: M-cat (32.7) ثم E-cat (30.3) ثم تكسير حراري (22.8). أعلى إنتاجيه للإيثلين (10.9) والبروبلين (15.7) تمت عند درجة حرارة 650° وعلى العامل الحفاز M-cat نتيجة لانتقائية الشكل والحمضية للعامل الحفاز. إنتاجية الجازولين على E-cat كانت أعلى بكثير من M-cat فمثلا عند درجة حرارة 550° كمية الجازولين على E-cat كانت 48.3 بالمئة بينما M-cat كانت 24.4 بالمئة. الفارق الكبير بين الحفازين يعزى الى محدودية الانتشار ل M-cat. أيضا تمت دراسة نسبة العامل الحفاز الى النفط الخام على التحويل والإنتاجيات، وقد أظهرت النتائج انه عند نسبة حفاز الى نفط أكثر من 4 فإن التأثير كان قليلا. وأخيرا تم أيضا دراسة تأثير الخلط الفيزيائي للعوال الحفازة عند نسب مئوية مختلفة وقد اتم استنتاج انه عند نسبة 30% M-cat ظهرت اعلى إنتاجية للألكينات. فإنتاجية الايثلين والبروبلين كانتا 9.9 و 19.2 بالمئة على التوالي.

أيضا تمت المقارنة بين قابلية التكسير للثلاثة أنواع من النفط العربي الخفيف. بالنسبة للتكسير الحراري عند درجة حرارة 650° فإن إنتاجية الايثلين والبروبلين كانت بالترتيب التالي: ASL (6.1 , 6.8 wt.%) ثم AXL (6.5 , 6.9 wt.%) ثم AL (7.6 , 8.6 wt.%). كمية انتاج الجازولين عند نفس درجة الحرارة كانت 48.0 و 38.1 و 34.4 لكل من AL, AXL, ASL على التوالي. التباينات الكبيرة في إنتاجية الجازولين والمركبات الثقيلة تنسب الي الفوارق في تركيب النفط الخام. بالنسبة للتكسير الحفزي فإن إنتاجية الايثلين والبروبلين كانت كالتالي: 25.8 للعربي الخفيف و 26.3 للعربي الشديد الخفة و 27.4 للعربي الخفيف جدا اعلى إنتاجية من الايثلين والبروبلين كانت 29.9 و 31.2 و 32.2 لكل من AL, AXL, ASL على التوالي وتم تحقيقها عند درجة حرارة 650° و نسبة حفاز الى نفط 6.

CHAPTER 1

INTRODUCTION

1.1 Background

Traditionally, refineries are used to produce transportation fuels, such as diesel and gasoline, whereas light olefins, particularly ethylene and propylene, have been considered as byproducts. On the other hand, refiners those days are in quest of developing new technologies that are capable of increasing production of light olefins and reducing the production cost, due to the current growth in demand for those valuables chemicals [1–3].

Within the most important petrochemicals are ethylene and propylene. Ethylene and propylene, are extensively used in an incredible number of products. For example, polyethylene, polypropylene, polyvinyl chloride, ethylene oxide, propylene oxide, styrene, and acrylonitrile [2,4]. In 2016, the global demand of ethylene and propylene was 150 and 100 million metric tons (MMT), respectively. Furthermore, in the same year the production of ethylene was 170 MMT and the production of propylene was 120 MMT. The annual growth in demand for both ethylene and propylene is considered among the top growth rates in petrochemical industry with rates of 3.6 and 4.0 % for ethylene and propylene, respectively. Due to this high growth in demand, by 2025 the global demand for ethylene and propylene is estimated to reach more than 200, and 140 MMT, respectively [2].

While propylene is produced via fluid catalytic cracking (FCC) units, steam cracking of naphtha, and new on-purpose technologies that are particularly designed to produce propylene, such as methanol to olefins, metathesis, coal to olefins, and dehydrogenation of propane, ethylene is produced from the steam crackers which use ethane, or naphtha as a feedstock [5]. Even though production of propylene via on-propose processes is increasing, those new technologies are not capable of meeting the increase in demand for propylene beside the high cost of production. Because of the flexibility of FCC unit, in the last three decades lots of modifications in operating conditions, catalysts, hardware, and recycling of naphtha have been applied to improve light olefins yields, especially propylene in addition to maintain gasoline production [1,6].

Production of naphtha and light olefins via the direct conversion of crude oil as a whole is anticipated to be the future of petrochemical industry. This new route has a potential of reducing cost of production, energy consumption and carbon emission, by reducing number of costly equipment. Moreover, some oil and chemical companies in Saudi Arabia, Indonesia, and China announced to build complexes that aims to directly convert crude oils as a whole to petrochemicals [1].

1.2 Olefins Demand and Supply

In 2016, total capacity of ethylene and propylene were 170 and 120 million metric tons (MMT), respectively with global demand of 150 MMT of ethylene and 100 MMT of propylene. The demand for both propylene and ethylene is estimated to grow fast, reaching more than 200 MMT and 140 MMT of ethylene and propylene, respectively, in 2025 with an annual growth rate of 3.6% for ethylene and 4.0% for propylene [1]. Figure 1 shows current and forecasted demand, production, and total capacity of ethylene and propylene, the graphs show a steady increase in all demand, production and total capacity. This huge rise is driven by the increased demand for ethylene and propylene derivatives, mainly polyethylene and polypropylene.

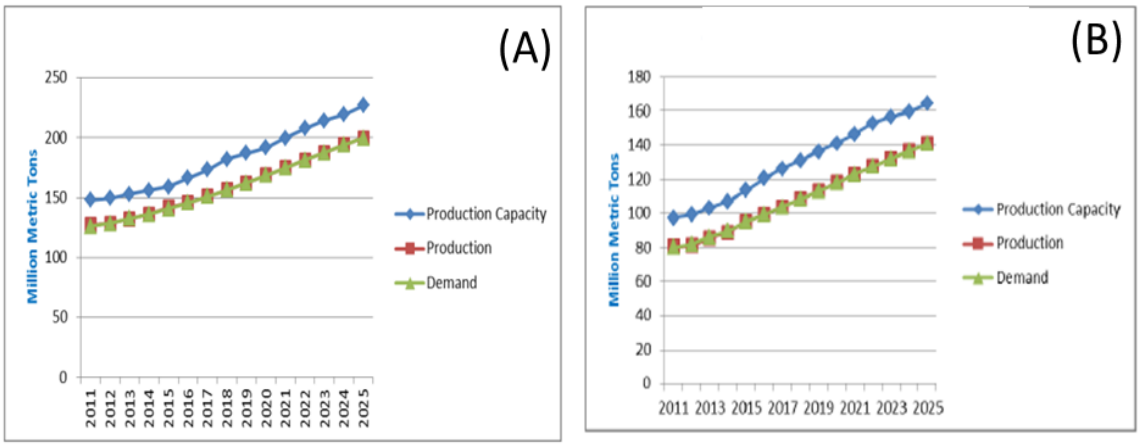

Figure 1 Global supply and demand of: (A) ethylene and (B) propylene [7]

As illustrated in Figure 2 most of ethylene production is centered in Middle East, USA and China with a production share of 19%, 18%, and 15%, respectively. On the other hand, for propylene production China is taking the lead with a production share of 26% followed by the USA (14%) and West Europe (13%). Table 1 presents production of ethylene and propylene in 2016 in million metric ton (MMT).

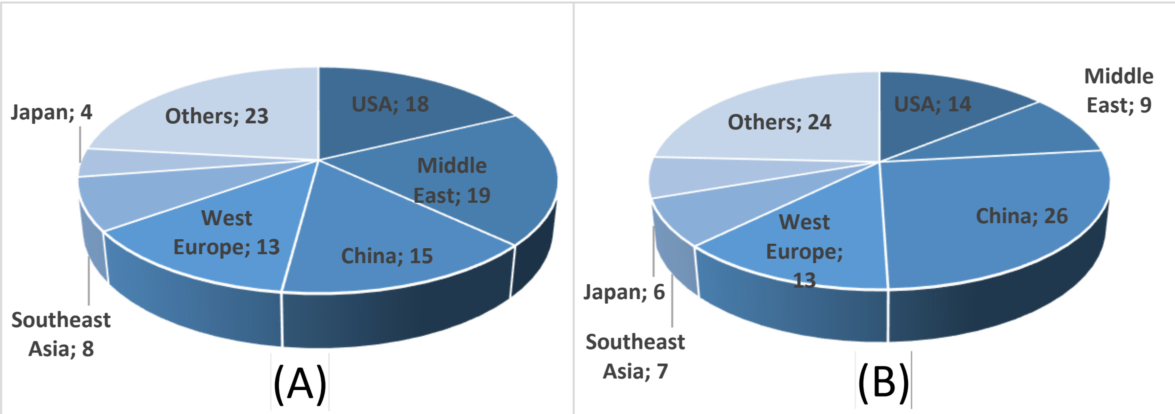

Figure 2 (A) Ethylene and (B) propylene production by region/country [7]

Table 1 2016 Ethylene and propylene production by country/ region, (MMT) [1]

Country /Region	Middle East	China	USA	Southeast Asia	Japan	West Europe	Others	World
Ethylene	28	22	26	11	6	19	34	146
Propylene	9	26	14	7	6	13	24	99
Total	37	48	40	18	12	32	58	245

1.3 Olefins Production

Light olefins can be produced via several processes, chose of process depends of feedstock availability, and products sought. The following process are the main ones:

- Steam cracking.
- Fluid catalytic cracking (FCC).
- Selective Dehydrogenation.
- Metathesis of olefins.
- Conversion of methanol to olefins (MTO and MTP).

For ethylene production steam cracking of either ethane or naphtha is the most widely used process. As shown in Figure 3 steam cracking of naphtha accounts for more than 43% of ethylene production and steam cracking of ethane has a share of around 36%. Furthermore, 9% of the produced ethylene is based on propane (around 13 MMT). Most of propylene is produced form steam crackers and fluid catalytic crackers. Nearly half of the propylene production is coming from the steam cracking process mainly steam cracking of naphtha. FCC units has the second largest share of propylene production with a share of 32%. Rest of propylene is produced by "on- purpose" processes. On-purpose processes include propane dehydrogenation (PDH), metathesis, Coal-to-Olefins(CTO) Methanol-to-Olefins (MTO) and Methanol-to-Propylene (MTP). Currently, on-purpose processes accounts for nearly 18% of the global propylene supply [1], [2].

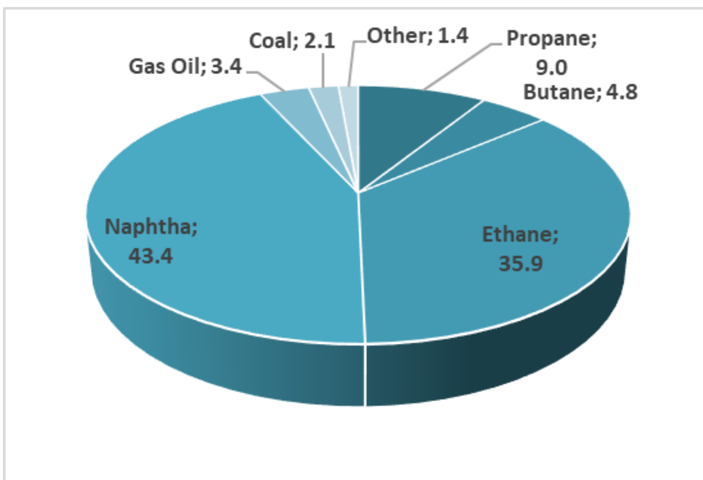

Figure 3 Ethylene production by feedstock, 2016 [1]

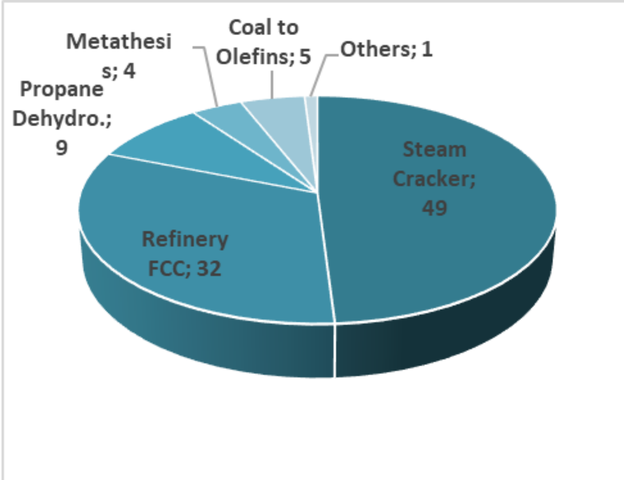

Figure 4 Propylene production by process, 2016 [1]

Steam cracking of ethane is the predominant process for ethylene production in Middle East and the United states due to the availability of natural gas, this process results in the highest profit margin. However, other regions which don't have natural gas, such as China, Japan, West Europe, and Southeast Asia produce ethylene via steam cracking of naphtha. Middle East, USA, and West Europe are the major consumers for propane and butane to produce ethylene. China is the main country that produces ethylene from coal.

Most of propylene produced in West Europe, Japan, and Southeast Asia is manufactured by steam crackers. China is mainly produces propylene by FCC units, steam crackers, and coal to olefins process. Propane dehydrogenation is mostly used in China, USA, and Middle East.

Figures 5 and 6 show ethylene and propylene production by region and feedstock.

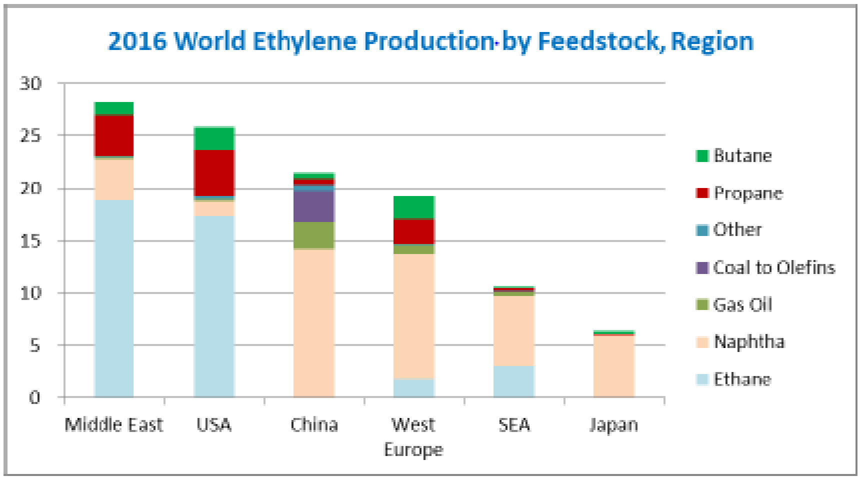

Figure 5 2016 Ethylene production (MMT) by feed and region [1]

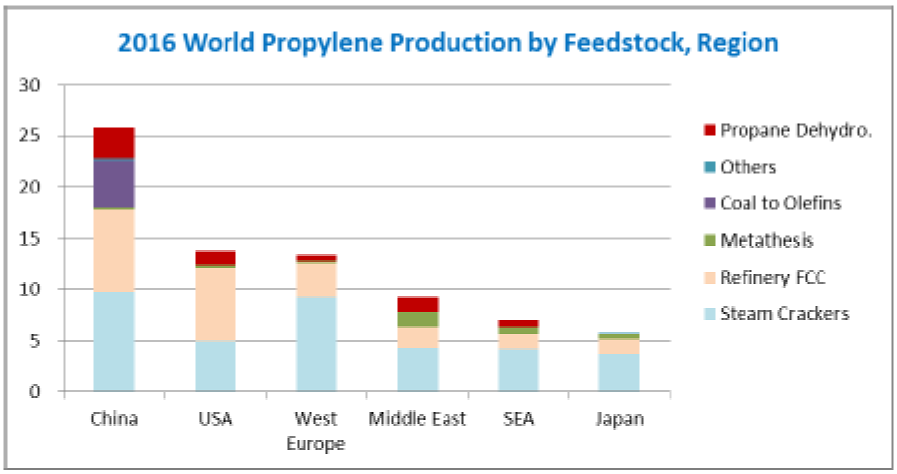

Figure 6 2016 propylene production (MMT) by feed and region [1]

1.4 Fluid Catalytic Cracking (FCC)

Due to the continuous growth in global demand of transportations fuels, diesel and gasoline, fuels' production must be enhanced. The FCC process plays a major role in the conversion of heavy oil fractions to lighter products and increase the production of transportations fuels and light olefins. In the coming two decades FCC process is expected to be used for cracking of biofuels and to decrease carbon dioxide emissions. FCC unit plays an important role in determining profitability of refineries. The first commercial FCC unit started operation in 1842, since that time lots of improvements have been implemented to the process to enhance the ability of fluid catalytic crackers to crack heavier and low value feedstocks and enhance the mechanical reliability. The FCC process has a successful history in adapting the continuous changes in market demand and feedstock. A micro-spherical catalyst is used in the FCC units that has a liquid like behavior when it is appropriately fluidized. Conversion of heavy oil fractions, typically vacuum gas oil to a higher-value transportations fuels, for example, gasoline, diesel, and jet fuel, is the main purpose of FCC unit [8–12]. The properties of feedstock will be discussed in section 1.6. Total processing capacity of FCC units exceeds 14.7 million barrels per day from nearly 350 crackers [13] around the world.

1.5 Process Description

Figure 7 shows a typical configuration of a refinery and how the FCC unit plays an important role the refinery [14]. Figure 8 illustrates the flow diagram of FCC unit.

Feed to the FCC unit is firstly diluted by steam to enhance aromatization then it is fed to the riser reactor with a regenerated catalyst. Then, the mixture flows upward and the cracking process take place in a short time (1-5 seconds). Cyclones are used to separate spent catalyst from the reaction mixture. Adsorbed heavy hydrocarbons on the catalyst are stripped by steam in the down-comer, also this added steam creates a buffer between oxidizing environment in the regenerator and the reducing environment in the riser. Spent catalyst in sent to a fluidized bed regenerator that is used to remove coke from catalyst by combustion with air. 5% of the fresh FCC catalyst is added to the process every day due to the limited life of the catalyst (around 30 days). Operating conditions for both the reactor and the regenerator are shown in Table 2.

Table 2 Typical operation conditions in FCC riser [15]

Variable	Value
Reactor Feed Rate, MBPSD	40
Feed Temperature, ºC	230
Catalyst/Oil Ratio	5.4
Catalyst Circulation Rate, tons/min	21.7
Catalyst Makeup Rate, tons/day	2.5
Riser Outlet Temperature, ºC	530
Dispersion Steam, wt.% feed	0.9
Stripping Steam, tons/ton catalyst	0.0213
Reactor Pressure, bar	2.0
Regenerator Pressure, bar	2.3
Regenerator Temperature, ºC	730
Flue Gas Temperature, ºC	735

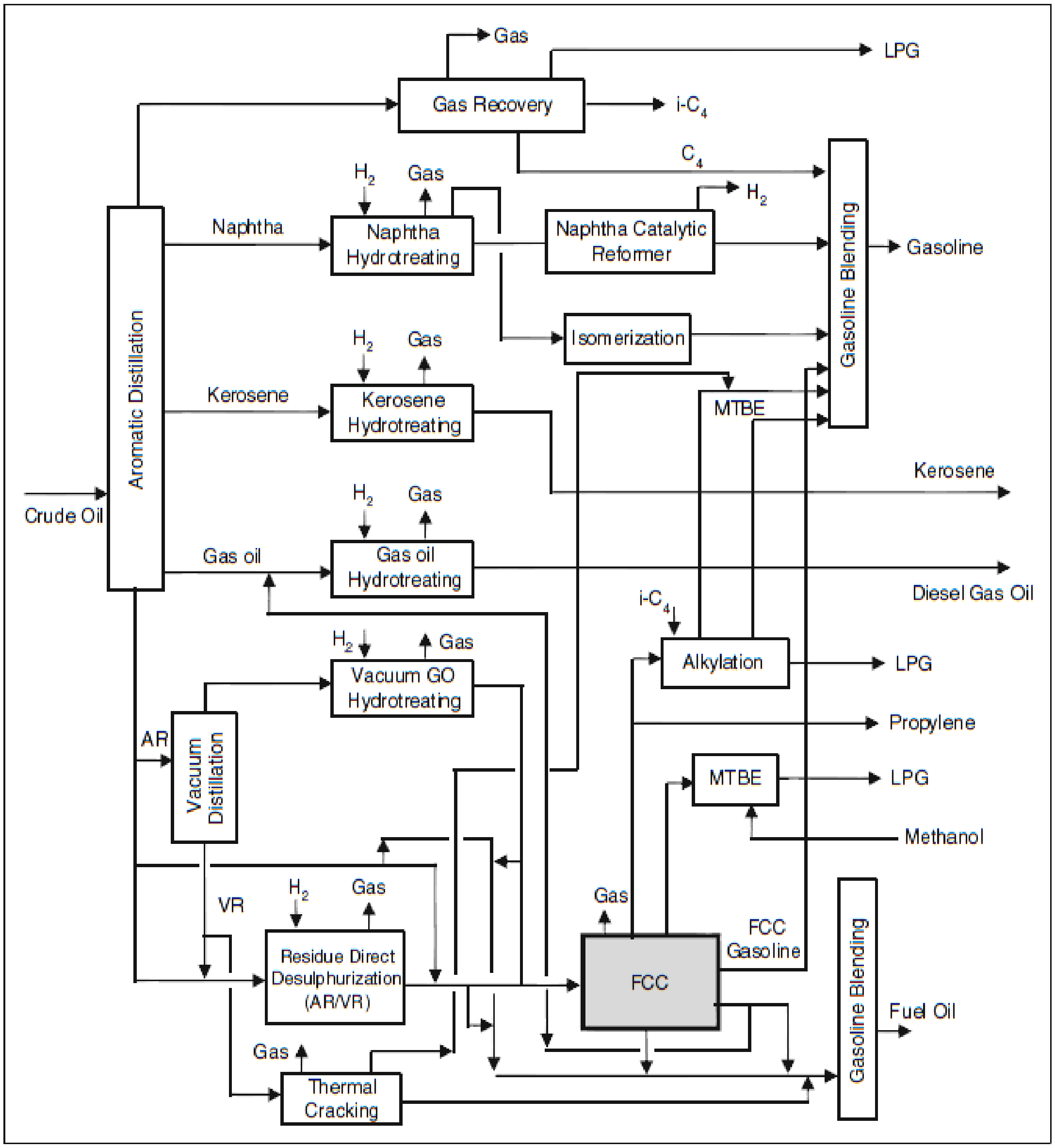

Figure 7 Role of FCC in refining operation [11]

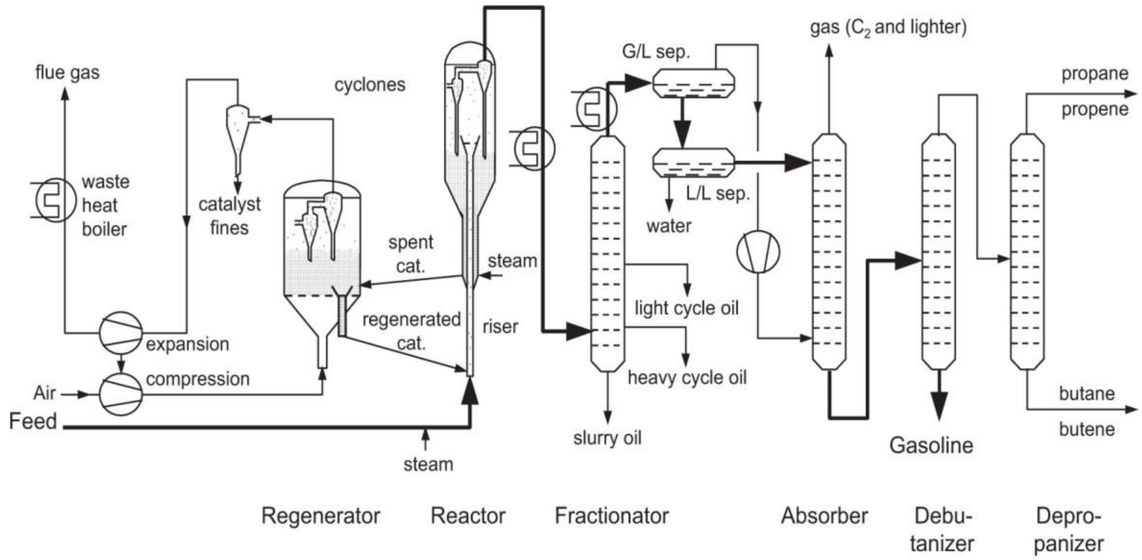

Figure 8 Flow scheme of a typical FCC unit [8]

1.6 Fluid Catalytic Cracking Feed and Products

Typical feeds to FCC units are an atmospheric or vacuum gas oils. But other heavy feeds can be processed. Gas oil is a mixture of paraffinic, aromatic, and naphthenic molecules. In addition to those main molecules, there are varying amounts of impurities, for example, metals, sulfur, and nitrogen. Each gas oil has its own contaminants and composition that may affect yields distribution. Feed pretreatment is essential in order to protect the catalyst and to improve cracking characteristics [9–11].

Residue and gas oil from conversion processes can be used as a feedstock to FCC units. Prior to catalytic cracking, feed must by hydrotreated in order to remove Sulphur and aromatics. The main limitation to feedstocks is metal contaminants and Conradson Carbon Residue (CCR). Conradson Carbon tends to deposit on the catalyst. This deposited carbon is difficult to be burned in the regenerator. For AR, prior to cracking it is first desulphurization in atmospheric residue desulfurizer. VR should also be desulfurized and may be de-asphalted. Tables 3 and 4 shows typical properties of feedstocks and products with their yield distribution and characteristics [11].

Table 3 Feedstock properties of FCC unit [14]

	Desulfurized VGO	AR
Specific gravity	0.896	0.889
API	26.3	27.5
Gas oil fraction, wt.% (<343 ºC)	7	4
VGO fraction (343-538 ºC)	88.5	52.5
VR fraction (>538ºC)	4.5	43.5
Conradson Carbon Residue, wt.%	0.2	4.2
Sulphur, wt.%	0.4	0.11
Nitrogen, wt.%	0.064	0.19
Nickel (Ni), ppm	0.26	17
Vanadium (V), ppm	0.15	0.5

Table 4 Products distribution of FCC unit[14]

Products	Yield (wt.%)	Characteristics
Dry gas +H_2S	3-5	H_2S must be removed
LPG	8-20	Petrochemical feedstock
Gasoline	35-60	Main product, good octane number
LCO	12-20	Rich in aromatics, high Sulphur content, diluent for fuel
HCO	10-15	Very rich in aromatics, slurry of solids, (mainly catalyst coke)
Coke	3-5	Consumed in regenerator

1.7 Thesis Objectives

The general objective of this study is to inspect the ability of producing light olefins by thermal and catalytic cracking of whole Arabian Light crude oil in MAT unit. The activity of several catalysts will be evaluated at different conditions (temperatures and catalyst to oil ratios). More specifically, this research will try to:

1. Investigate thermal and catalytic crackability of Arabian Light Crude oil.
2. Enhance light olefins' yield from catalytic and thermal cracking of Arabian Light crude oil that can be further used in petrochemical industries
3. Convert Saudi Arabian light Crude into valuable products.
4. Analyze the effect and activity of different catalysts.
5. Compare the crackability of different types of light crude oil.

1.8 Thesis Scope

Second chapter provides background information about FCC catalysts and additives. In addition, catalyst evaluation parameters will be discussed. Furthermore, a comprehensive literature review about thermal and catalytic cracking of whole crude oil is provided.

Third chapter gives an overview about feedstocks and materials used in this work. In addition, specifications and operation of MAT unit are illustrated. Furthermore, analysis of products and instruments used will be explained.

Fourth chapter presents thermal and catalytic cracking of AL crude oil. First, a comparison between thermal and catalytic cracking is shown and compared at constant conversion and temperature. Then, the effect of temperature, catalyst to oil ratio, and mixing catalysts are discussed.

Fifth chapter compares the crackability of three different crude oils, ASL, AX and AL, as thermal and catalytic. Firstly, a thermal cracking is investigated, and the product yields obtained from the three crude oils are compared. Secondly, the effect of catalyst and mixed catalyst is analyzed for the three crude oils. Lastly, the effect of catalyst to oil ratio is investigated over the optimum catalyst.

Sixth chapter summarizes findings of this research and lists some recommendations for future work.

CHAPTER 2

LITERATURE REVIEW

2.1 Background

This chapter provides background information about FCC catalysts and role of ZSM-5 zeolite. It also explains all mechanisms, chemistry and thermodynamics of thermal and catalytic cracking reactions. In addition, some catalyst evaluation parameters will be explained. Lastly, an information about the cracking of crude oil as a whole are summarized from previous work.

2.2 Fluid Catalytic Cracking Catalysts

Introducing zeolites to FCC catalyst in 1960s was among the top developments in history of cracking. Those zeolite-based catalysts showed with a little capital investment a higher profit can be made. Lots of improvements have been implemented to the FCC catalysts to meet the market demands and accommodate the changing feedstock while keeping minimum capital investments. Zeolite catalysts have more activity and selectivity in comparison to silica-alumina catalysts.

FCC catalyst is composed of two main components which are zeolite and matrix. In some cases, a third one is added to the catalyst and it is called additive/additives. Additives are used to increase catalyst resistance to metals form the feed, boost octane number of gasoline, facilitate CO oxidation, reduce SO emissions, or enhance olefins production [16].

Three types of zeolites are used in FCC catalysts which are Type Y, Type X and ZSM-5. Both zeolites X and Y have a similar crystalline structure. Y zeolite has a higher silica-to-alumina ratio. Moreover, Y zeolite has a higher hydrothermal and thermal stability than Y zeolite. Earlier FCC catalysts were containing X zeolite, however, almost all current FCC catalysts contains zeolite of type Y. Figure 9 shows the structure of zeolites of type Y and X.

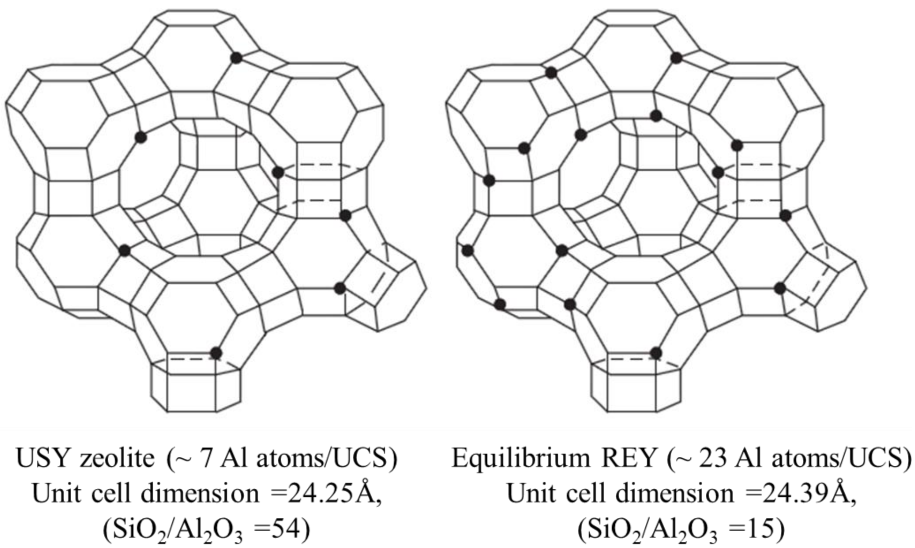

Figure 9 Geometry of USY and REY zeolites [9]

In 1986, a reduction is lead in gasoline is started which resulted in a necessity for a higher octane FCC gasoline. Catalysts producers responded by an adjustment for the zeolites. The change involved was reducing the number of aluminum atoms from the zeolite framework. Removing aluminum atoms resulted in decreasing total potential acidity per unit cell, increasing silica-to-alumina ratio and decreasing sodium level. Those changes increased olefinicity which raised gasoline octane. This newly formed zeolite was named ultra-stable Y (USY) zeolite due to its higher stability than conventional Y zeolite [9,11].

Y-zeolite is the key ingredient in FCC catalyst. Y-zeolite is a crystalline aluminosilicates that has a Y-faujasite structure as shown in Figure 9 the largest pore size in the Y-zeolite is 8^{o} A that is named the super cage which can accommodate large compounds up to C_{25} [11]. Commercial FCC catalyst contains 10-50% zeolite. The percentage of the zeolite is affecting catalytic activity and selectivity of the catalyst [16].

Another zeolite that can be used in FCC catalyst either as zeolite or additive is ZSM-5 (MFI) which is a versatile zeolite that enhances yield of olefins and boost the octane rating. It will be further discussed in the following section.

Matrices which are composed of natural and synthetic component are added to the FCC catalyst to spread out the zeolite, improve the properties of the catalyst, and it may have some catalytic impacts. Matrices have three components which are:

1. Filler which is used to make the body of the catalyst. The most common filler is clay, it is natural component.
2. Binder that is added to the catalyst to act as a glue to provide cohesion between zeolite particles. The importance of binder and filler is to give physical integrity to the catalyst (attrition resistance and density).
3. Additives are also added in terms of small amounts of metals (ppm) to enhance combustion of carbon monoxide in the regenerator. Furthermore, metallic oxides are used to fix SO_x on the surface of the catalyst, then the sulfur is recovered in the reactor as H_2S [11].

The ratio of zeolite to matrix in FCC catalyst plays an important role in products distribution. For example, the product yield of C_3/C_4 increased from 12 wt.% to 15 wt.%

as the ratio of zeolite to matrix decreased from 4 to 0. However, the gasoline yield decreased [16]. Typical FCC catalyst's compositions are shown in Figure 10.

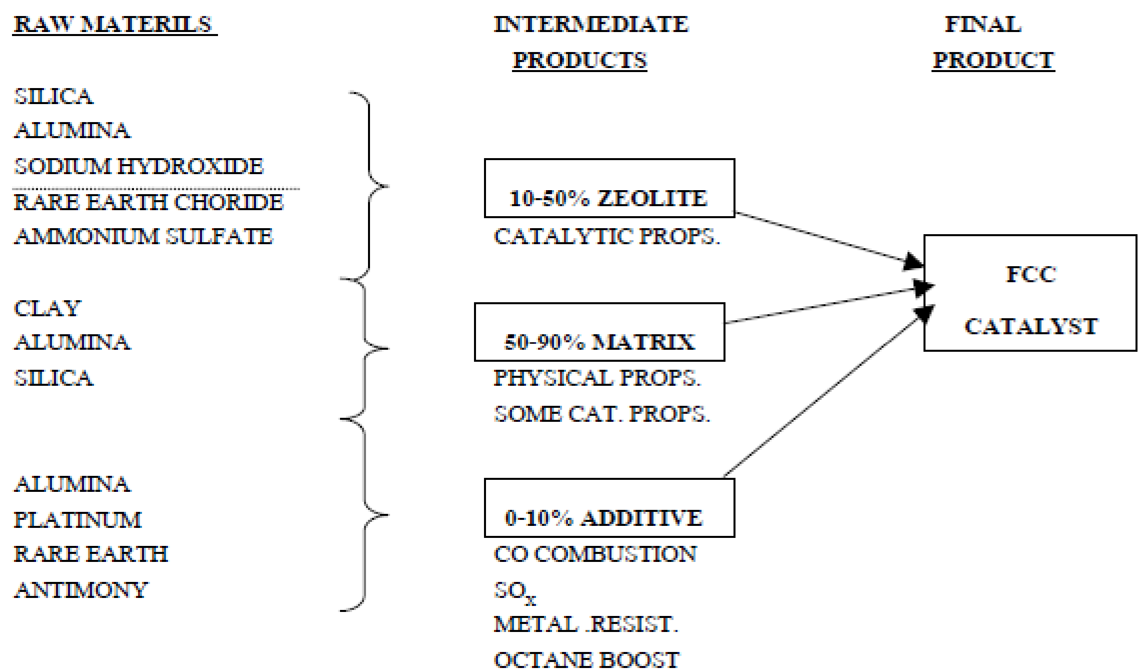

Figure 10 Composition of a typical FCC catalyst

2.3 ZSM-5 as an Additive to Enhance Propylene Yield

Production of larger amounts of lower olefins (ethylene and propylene) can be achieved by the addition of a small amount of ZSM-5 (Zeolite Synthesized by Mobil, Figure 11) zeolite to the conventional Y zeolite catalyst [17,18]. ZSM-5 has narrower pores and thus are only accessible to linear or slightly branched paraffins and olefins and not to the highly branched ones and aromatic compounds, as illustrated in Figure 12. Therefore, low-octane naphtha-range hydrocarbons in particular are cracked in ZSM-5 pores. Accordingly, gasoline obtained has a higher octane number, although at the expense of gasoline yield.

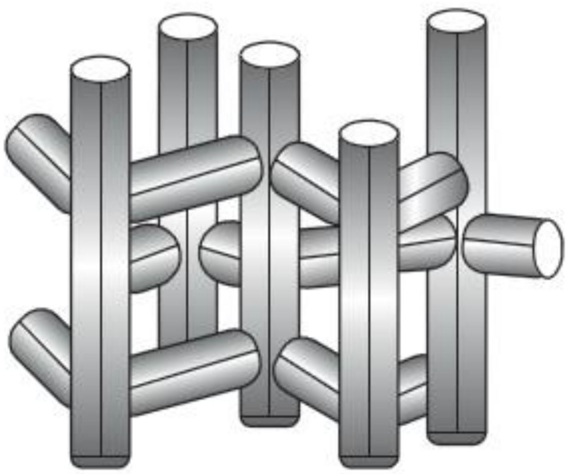

Figure 11 ZSM-5 zeolite, 5.1– 5.6 Å channel opening [9]

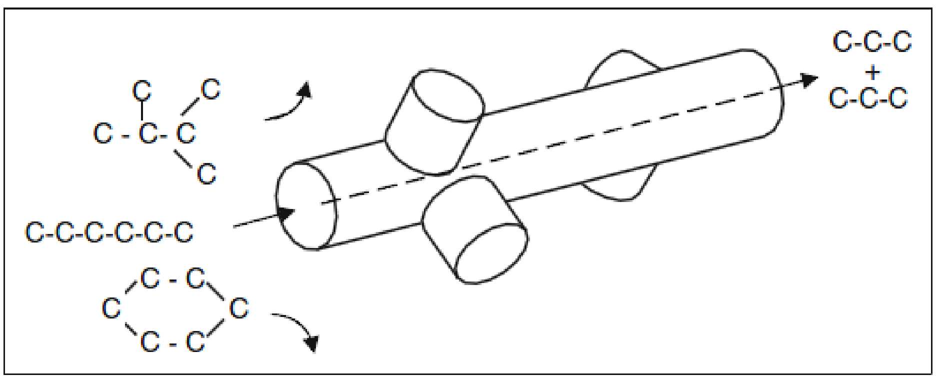

Figure 12 Shape-selective cracking with ZSM-5 zeolite[16]

2.4 Mechanisms and Thermodynamics of Cracking Reactions

The reactions in the FCC unit are complex due to the huge number of compounds available in the feed and products that act as an intermediate sometimes. Table 5 shows reactions that take place in the FCC reactor. The products yield depends on many factors, such as, strength and nature of the catalyst and acid sites. Even though most of reactions are catalytic, some thermal reactions also take place. The main reasons for thermal cracking are: the nonideality in mixing in the riser and the poor separation in the reactor of cracked products. Whether catalytic or thermal cracking, hydrocarbons cracking is about the breakage of carbon-carbon bond. But they (thermal and catalytic cracking) proceed via different routes and their product yields are different.

Table 5 Important reactions occurring in the FCC unit [9]

1.	Cracking:	
	Paraffins cracked to olefins and smaller paraffins	$C_{10}H_{22} \rightarrow C_4H_{10} + C_6H_{12}$
	Olefins cracked to smaller olefins	$C_9H_{18} \rightarrow C_4H_8 + C_5H_{10}$
	Aromatic side-chain scission	$ArC_{10}H_{21} \rightarrow ArC_5H_9 + C_5H_{12}$
	Naphthenes (cycloparaffins) cracked to olefins and smaller ring compounds	Cyclo-$C_{10}H_{20} \rightarrow C_6H_{12} + C_4H_8$
2.	Isomerization:	
	Olefin bond shift	1-$C_4H_8 \rightarrow$ trans-2-C_4H_8
	Normal olefin to iso-olefin	n-$C_5H_{10} \rightarrow$ iso-C_5H_{10}
	Normal paraffin to isoparaffin	n-$C_4H_{10} \rightarrow$ iso-C_4H_{10}
	Cyclohexane to cyclopentane	$C_6H_{12} + C_5H_9CH_3$
3.	Hydrogen transfer:	Naphthene + olefin $\rightarrow$ aromatic + paraffin
	Cycloaromatization	$C_6H_{12} + 3C_5H_{10} \rightarrow C_6H_6 + 3C_5H_{12}$
4.	Transalkylation/alkyl-group transfer	$C_6H_4(CH_3)_2 + C_6H_6 \rightarrow 2C_6H_5CH_3$
5.	Cyclization of olefins to naphthenes	$C_7H_{14} \rightarrow CH_3$-cyclo-$C_6H_{11}$
6.	Dehydrogenation	n-$C_8H_{18} \rightarrow C_8H_{16} + H_2$
7.	Dealkylation	Iso-C_3H_7-$C_6H_5 \rightarrow C_6H_6 + C_3H_6$
8.	Condensation	Ar-$CH{=}CH_2 + R_1CH{=}CHR_2 \rightarrow$ Ar—Ar $+ 2H$

Thermal cracking:

Temperature and residence time are the main factors in thermal cracking. Thermal cracking occurs when hydrocarbons are exposed to high temperatures (550-650 ºC) [9].

Formation of free radicals is the initial step in thermal cracking. They are formed by the cleavage of C-C bond which results in formation of two free radicals. The following equation shows this reaction:

$$R_1 - \underset{\displaystyle H}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}} - \underset{\displaystyle H}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}} - R_2 \rightarrow R_1 - \underset{\displaystyle H}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C^{\bullet}}}}} + \underset{\displaystyle H}{\overset{\displaystyle H}{\underset{|}{\overset{|}{{}^{\bullet}C}}}} - R_2 \qquad (2.1)$$

Free radicals are very reactive and have a short life time, so they are further reacted via beta-scission, alpha-scission, and polymerization. Beta-scission is a break two carbon away from the free radical; Alpha-scission, one carbon away. Beta-scission results in olefins production (ethylene) and a primary free radical as shown in the next equation[19]:

$$R-CH_2-CH_2-{}^{\bullet}C-H_2 \rightarrow R-{}^{\bullet}C-H_2 + H_2C{=}CH_2 \tag{2.2}$$

The resultant free radical form the last equation can further undergo beta-scission to produce more ethylene.

Alpha-scission is not favored from a thermodynamic point of view, but it occurs. Alpha-scission results in a methyl radical that in further saturated to form methane a secondary or tertiary free radical (following equation).

$$\begin{aligned} &H_3C^{\bullet} + R-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3 \\ &\rightarrow CH_4 + R-CH_2-CH_2-CH_2-CH_2-{}^{\bullet}CH-CH_2-CH_3 \end{aligned} \tag{2.3}$$

This radical can further undergo beta-session which produce a primary free radical and an alpha-olefin according to the following equation:

$$\begin{aligned} &R_1-{}^{\bullet}CH_2 + R-CH_2-CH_2-CH_2-\ CH_2-CH_2-CH_2-CH_3 \\ &\rightarrow R-CH_3 + R-CH_2-CH_2-CH_2-CH_2-CH_2-{}^{\bullet}CH-CH_3 \end{aligned} \tag{2.4}$$

$H_3{}^{\bullet}C$ is less stable than $R-{}^{\bullet}CH_2$. Consequently, the rate of extracting of hydrogen of $H_3{}^{\bullet}C$ is higher than of $R-{}^{\bullet}CH_2$.

This reaction sequence results in a product that is rich in C_1-C_2 and a fair yield of alpha-olefins.

Among the disadvantages of thermal cracking is that large percentage of olefins that formed are further polymerized and condensed to from coke. **Table 6** shows how thermal and catalytic cracking are different in terms of product distribution.

Table 6 Comparison of products between catalytic and thermal cracking [20]

Hydrocarbon Type	Thermal Cracking	Catalytic Cracking
n-Paraffins	C_2 is major product, with much C_1 and C_3, and C_4 to C_{16} olefins; little branching	C_3 to C_6 is major product; few *n*-olefins above C_4; much branching
Olefins	Slow double-bond shifts and little skeletal isomerization; H-transfer is minor and nonselective for tertiary olefins; only small amounts of aromatics formed from aliphatics at 932°F (500°C)	Rapid double-bond shifts, extensive skeletal isomerization, H-transfer is major and selective for tertiary olefins; large amounts of aromatics formed from aliphatics at 932°F (500°C)
Naphthenes	Crack at slower rate than paraffins	If structural groups are equivalent, crack at about the same rate as paraffins
Alkyl-aromatics	Crack within side chain	Crack next to the ring

Catalytic cracking:

The major reaction that occur in the FCC reactor is catalytic cracking of paraffins, naphthenes, olefins, and side chains in aromatics. Figure 13 illustrates the network of reactions that take place in the reactor. As shown in the figure, catalytic cracking can be categorized into two classifications:

Primary cracking: that mainly produces gasoline and LCO.

Secondary cracking: re-cracking and rearrangement of cracked products.

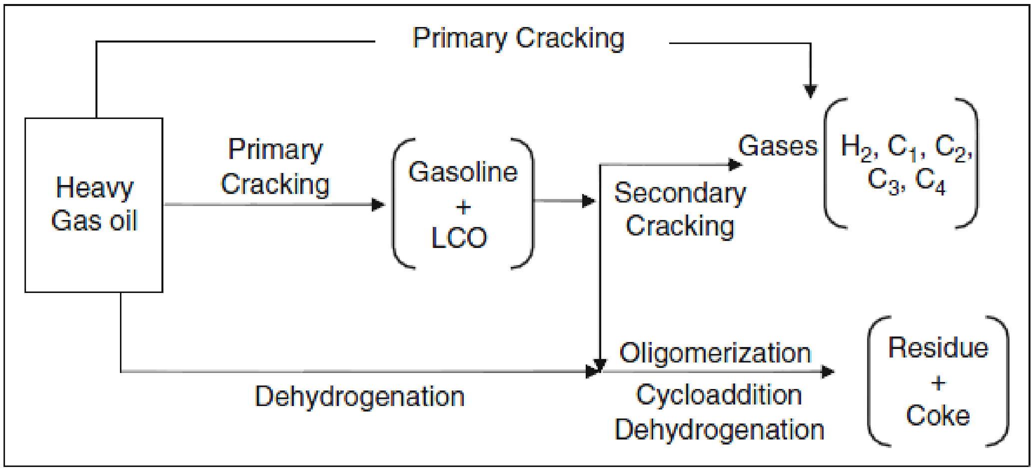

Figure 13 FCC reactions network [11]

Primary cracking:

Primary cracking reaction occur via the carbenium ion intermediates as illustrated in the following steps:

(1) formation of olefin from paraffin by the mild thermal cracking:

$$nC_8H_{18} \rightarrow CH_4 + CH_3 - (CH_2)_4 - CH = CH_2 \qquad (2.5)$$

(2) Carbenium ion formation, $R\text{-}CH_2^+$

(a) at Bronsted site:

$$R{-}CH{=}CH{-}CH_2{-}CH_2{-}CH_3 + H^+ \rightarrow R{-}C^+H{-}CH_2{-}CH_2{-}CH_2{-}CH_3 \qquad (2.6)$$

(b) at Lewis site:

$$R{-}CH_2{-}CH_2{-}CH_2{-}CH_3 \rightarrow R{-}C^+H{-}CH_2{-}CH_2{-}CH_3 \qquad (2.7)$$

Both Lewis and Bronsted sites are available on the catalyst to generate carbenium ions. Lewis site extracts two pair of electrons from a paraffin. On the other hand, Bronsted site donates a proton to an olefin that is formed by thermal cracking [9,11].

Once carbenium ions are formed they undergo many reactions. The strength and nature of acidic sites affect which reaction and to what extent they will occur. The three main reactions are:

1. Beta-session.
2. Isomerization.
3. Hydrogen transfer.

(1) Beta-scission:

Beta-session is the splitting of C-C bond two carbons away from the carbenium ion. Breaking at beta location is more favorable than alpha location since less energy is required. Furthermore, long-chain hydrocarbons are more reactive than short-chain hydrocarbons. Moreover, the cracking rate increases with increasing chain length.

An olefin and a newly formed carbenium ion are the initial products of beta-session (following equation). The newly formed carbenium ion will further continue a series of chain reaction until the carbenium ion has 4-5 carbons which is difficult to crack. So, the positive change will be transferred to another large hydrocarbon which can crack.

$$\begin{aligned} &R{-}C^{+}H{-}CH_2{-}CH_2{-}CH_2{-}CH_3 \\ &\rightarrow CH_3{-}CH{=}CH_2 + C^{+}H_2{-}CH_2{-}CH_2R \end{aligned} \tag{2.8}$$

Cracking is favored by high temperature since cracking is endothermic and beta-session is monomolecular. In addition, cracking is not equilibrium limited.

The termination of the chain reaction is happened when: (1) the carbenium is converted into an olefin by losing its proton to the catalyst. (2) the carbenium is converted into a paraffin by picking up a hydride ion.

(2) Isomerization:

Isomerization reactions happen commonly in catalytic cracking and less commonly in thermal cracking. For both thermal and catalytic cracking, cleavage of C-C bind is by beta-session. In thermal cracking, free radicals produce normal hydrocarbons. For catalytic cracking, carbenium ions tend to rearrange to form tertiary ions since they are more stable than primary and secondary ions, they shift around and crack to yield branched molecules:

$$CH_3-CH_2-C^+H-CH_2-CH_2R \rightarrow \begin{array}{c} CH_3-\underset{\substack{|\\ H}}{C^+}-\underset{\substack{|\\ CH_3}}{CH}-CH_2R \\ \text{or} \\ C^+H_2-\underset{\substack{|\\ CH_3}}{CH}-CH_2-CH_2R \end{array} \qquad (2.9)$$

Isomerization reactions have the following advantages:

- Gasoline with high octane rating, since iso-paraffins have higher octane than normal ones.
- High-value oxygenate and chemical in C_3/C_4 fraction. Isoamylene and isobutylene are used to produce tertiary amyl methyl ether (TAME) and methyl tertiary butyl

ether (MTBE). TAME and MTBE are added to the gasoline pole to reduce auto emissions.

- Less cloud point in the diesel fraction, since the cloud point of LCO fraction is improved by the enhancement in iso-paraffins.

(3) Hydrogen transfer (HT) reactions:

Hydrogen transfer is a bimolecular reaction where an olefin is one of reactants. Reactants can be two olefins or an olefin and a naphthene. For the reaction of two olefins, both reactants must be adsorbed to active sites where they are in close proximity. As hydrogen is transferred from a molecule to another, one of the two olefins becomes a cyclo-olefin and the other becomes a paraffin. Cyclo-olefin also transfer hydrogen with another olefin to produce a cyclo-diolefin and a paraffin. Finally, an aromatic is formed by the rearrangement of the cyclo-diolefin. Due to the high stability of aromatics, the reaction chain will stop. The following equation illustrates the hydrogen transfer of olefins to produce aromatics and paraffins:

$$\begin{array}{ccccc} 4C_nH_{2n} & \rightarrow & 3C_nH_{2n+2} & + & C_nH_{2n-6} \\ \text{olefins} & \rightarrow & \text{paraffins} & + & \text{aromatic} \end{array} \tag{2.10}$$

The other hydrogen transfer reaction is between olefins and naphthenes. Naphthenes compounds donates hydrogen to olefins to yield aromatics and paraffins according to the following equation:

$$\begin{array}{ccccccc} 3C_nH_{2n} & + & C_mH_{2m} & \rightarrow & 3C_nH_{2n+2} & + & C_mH_{2m-6} \\ \text{Olefin} & & \text{Naphthene} & & \text{Paraffin} & & \text{Aromatic} \end{array} \tag{2.11}$$

Gasoline yield and stability are usually increased by HT reactions. Due to the lower production of olefins, gasoline ha a reduced reactivity [9]. In addition, HT reactions reduce secondary reactions of gasoline since olefins are the reactive species [11].

Hydrogen transfer reactions has the following disadvantages:

- Less olefin yield in LPG.
- Gasoline with lower octane.
- Less olefins in front cut of gasoline.
- More aromatics in gasoline.

Other reactions:

Hydrogen transfer, cracking and isomerization accounts for the majority of catalytic cracking. There are other reactions which plays an important role in unit operation, such as dehydrogenation and coking.

Dehydrogenation reactions take place only if catalysts are contaminated with metals, for example, vanadium and nickel.

Mechanisms of forming coke are not very well understood and complex. Similar to HT reactions, coke formation is a bimolecular reaction. It proceeds by free radicals or carbenium ions mechanisms. As HT rate increases, coke yield also increases. It’s assumed that reactions yielding multiring aromatics and unsaturates are the principle coke forming hydrocarbons. Unsaturates such as multiring olefins, diolefins and olefins are extremely reactive and may produce coke via polymerization [9,11].

Secondary cracking:

The produced gasoline from the primary reactions can be further reacted in secondary cracking, that is mainly occurred by the HT mechanisms, for example, cyclisation, isomerization, and formation of coke.

Thermodynamics aspects:

The most important reaction in catalytic cracking is beta-session which is not equilibrium limited; therefore, thermodynamics are limited value in either adjustment of operating conditions or estimation of extent of reaction. Cracking of long chain olefins and paraffins reach up to 95% completion at cracking conditions.

Some HT reactions perform in the same manner, dehydrogenation, isomerization, dealkylation, and transalkylation reactions are intermediates in equilibrium attaining. Condensation reactions, such as paraffin alkylation and olefin polymerization are less favorable at high temperatures. Table 7 shows heat of reaction and equilibrium constants of those reactions. It’s clear that magnitude and type of those reactions have an effect on energy balance and operation of the unit. For instance, the net heat of reaction will be more endothermic if a catalyst with less HT characteristics is used. Accordingly, this will involve larger circulation of catalyst and higher coke yield in order to maintain the energy balance. [9,11,20]

Table 7 Typical thermodynamic data for idealized reactions of importance in catalytic cracking [20]

Item		$LogK_E$ equilibrium constant			Heat of reaction KJ/mole
Reaction/Temperature (°C)		450	510	530	510
Cracking	n-$C_{10}H_{22}$ → n-C_7H_{16} + C_3H_6	2.04	2.46	–	33815
	1-C_8H_{16} → 2C_4H_8	1.68	2.1	2.23	35516
Hydrogen transfer	4C_6H_{12} → 3C_6H_{14} + C_6H_6	12.44	11.09	–	115720
	cyclo-C_6H_{l2} + 3 l-C_5H_{10} → 3n-C_5H_{12} + C_6H_6	11.22	10.35	–	77282
Isomerization	l-C_4H_8 → trans-2-C_4H_8	0.32	0.25	0.09	-5142
	n-C_6H_{10} → iso-C_6H_{10}	-0.2	-0.23	-0.36	-3608
	o-$C_6H_4(CH_3)_2$ → m-$C_6H_4(CH_3)_2$	0.33	0.3	–	-1382
	cyclo-C_6H_{l2} → CH_3-cyclo-C_5H_9	1	1.09	1.1	6609
Transalkylation	C_6H_6 + m-$C_6H_4(CH_3)_2$ → 2$C_6H_5CH_3$	0.65	0.65	0.65	-233
Cyclisation	l-C_7H_{14} → CH_3-cyclo-C_6H_{11}	2.11	1.54	–	-40071
Dealkylation	iso-C_3H_7-C_6H_5 → C_6H_6 + C_3H_6	0.41	0.88	1.05	42838
Dehydrogenation	n-C_6H_{14} → l-C_6H_{12} + H_2	-2.21	-1.52	–	59092
Polymerization	3C_2H_4 → l-C_6H_{12}	–	–	-1.2	-
Paraffin alkylation	l-C_4H_8 + iso-C_4H_{10} → iso-C_8H_{18}	–	–	3.3	-

The occurrence of endothermic and exothermic reactions contributes to the overall energy balance. The overall reaction is endothermic, and heat is provided via the combustion of coke during the regeneration of the catalyst.

A low operating pressure (1-5 bars) is required due to the large volume of cracked products. In addition, a high operating temperature is required due to the endothermic nature of the cracking reactions [11].

2.5 Catalyst Evaluation Parameters

To evaluate the performance of cracking, some parameters will be considered, such as conversion and HTC (hydrogen transfer coefficient). Another important parameter is the

CMR (cracking mechanism ratio). Also, the ratio of propylene to ethylene (P/E) was considered [21–23]:

- Conversion can be defined in many ways, in this study it will be defined as the percentage of gas and coke produced.
- HTC can be defined as the ratio of yield of butanes to butenes. It indicates the tendency of the catalyst to perform HT reactions[24]. HT reactions produce paraffins by consuming light olefins. So, if light olefins are desired, low HTC is required.
- The cracking mechanism ratio (CMR) is ratio of dry gas to isobutane. The CMR is an important parameter to disclose is a qualitative manner the extent to which the two acid catalyzed cracking mechanism occurs either as beta-session cracking or as a protolytic cracking [1].

2.6 Whole Crude Oil Cracking

Whole crude oil is that crude oil that is produced from the oil wells and was undergone some treatment like desalting. Crude oil is used as a feedstock to distillation units at refineries. Crude oil can be used as feedstock to the fluid catalytic cracking units to meet the huge demand for light olefins mainly ethylene and propylene. By this process the need to distillation units is eliminated and hence reduce the cost.

A new attractive route to produce light olefins and gasoline is the direct conversion of crude oil to chemicals which can bypass some of the refining steps that have a high cost [25]. This new emerging process is attractive in terms of lowering the feedstocks price, increasing profit margin, reducing the energy consumptions, and lowering the carbon dioxide emissions. Furthermore, the higher stability in petrochemicals prices compared to transportation fuels make it more convenient to convert the crude oil to petrochemical than transportation fuels. With the current developments in catalytic technology, the direct conversion of crude oil to petrochemicals and fuels can be achieved by applying some configurations to the modern complex refineries. The direct conversion of crude oil to light olefins and gasoline have been investigated by some oil and chemical companies. For example, in 2014 ExxonMobil commercialized an oil to petrochemicals plant which produce light olefins via steam cracking of light crude oil. Recently, the construction of crude to chemicals plant was announced in several countries, such as Saudi Arabia, China, and Indonesia [2,26].

Fitzharris and his colleges in in U.S. Patent No. 4859310 1989 proposed a new technology for catalytic cracking of crude oil. Their technology includes desalting process that is followed by preheating of the crude to 221 ºC. after that the crude was sent to a flash drum to separate the vapor and the liquid phases. Then, the liquid product was sent to a FCC unit [27]. The temperature in the raiser reactor was in the range of 482 to 551ºC and zeolites or aluminosilcates can be used as a catalyst. The products from this process include Decanted Oil, Light Cycle Oil, and light hydrocarbons. This technology showed a cost effective method for refining of crude oil in comparison to the conventional FCC process [27].

Bryden and his coworkers investigated using shale oil as a feedstock to an FCC unit. The crude they used has an API of 42º, and 0.19% Sulphur. The used catalyst was commercial zeolite that has a BET surface area of 196 m^2/g. the catalyst to oil ratio was 6. A conversion of 83.5 wt.% was achieved at 526 ºC by ACE reactor. They defined conversion as (100 – LCO-Bottoms). The yield of coke was small also the bottoms[28].

As shown in table 8, thermal and catalytic cracking of different types of crude oil have been investigated by Al-Khattaf and his colleagues via advanced catalytic evaluation (ACE), riser simulator, and Micro-Activity Test (MAT) unit [1,2,29,30]. Their results showed a high potential for the cracking of crude oil as a whole via FCC catalysts and ZSM-5 towards light olefins and gasoline. A method for the conversion of crude oil to was disclosed by Powers in U.S. Patent No. 7019187 2006 [31]. Powers method suggests to mild-catalytic crack the crude oils at the bottom of the furnace at a temperature enough to vaporize the crude. After that, the vapor is thermally cracked in the radiant section at the top of the furnace.

Schrod et al. disclosed in US Patent 0267745 2013 [32] a process for production of hydrocarbon chemicals form crude oil. They proposed to separate the crude, via an atmospheric distillation, into three streams which are gas, liquid and residue fraction. Then, the gas will be steam cracked and the liquid will be further separated and catalytically cracked. A similar work was reported by Abba et al.in US Patent 9228140 2016 [33] an integrated hydro-processing, steam pyrolysis and catalytic cracking process to produce light olefins and aromatics from Arabian Light crude oil. Firstly, the crude is hydro-processed then the light fraction is steamed cracked while heavy fraction is catalytically cracked. Another reported work that was disclosed by Bourane et al. in U.S. Patent No. 9290705 2016 [34] for the development of a high-severity process for catalytic cracking of crude oil to light olefins and other products. They suggested to separate the crude oil into two fractions depending on boiling points. After that, both fractions will be cracked in a down-flow FCC unit separately. All the catalyst for both reactors will be regenerated in a common vessel. They reported that the yields of ethylene and propylene were 5.2 and 15.8

wt.% respectively, for catalytic cracking of Arab Extra Light crude oil at a catalyst to oil (C/O) ratio of 31 and a temperature of 600 ºC [34].

Table 8 Previous work done for crude oil cracking

Reactor	**Feed**	**Temperature (°C)**		**Max. $C_3^=$**	**Max. $C_2^=$**	**Thermal cracking**	**Reference**
2 Separate downers	AXL	600 heavy fraction	640 light fraction	**15.8**	**5.2**	No	[34]
MAT	ASL	550		**7.7**	**2.5**	No	[30]
	AXL			**10.3**	**3**		
	AL			**9.7**	**3.3**		
MAT	AXL	550		**13.8**	**4.3**	No	[29]
Riser simulator	ASL	500-575		**12.3**	**6.6**	No	[2]
MAT	ASL	550-600		**14.2**	**5.7**	Yes	[1]
ACE		550-650		**16.3**	**8**		

The previous discussions showed that there is no thermal cracking investigation, except for ASL crude oil. In addition, catalytic cracking of AL crude oil was only examined at 550 ºC. So, a detailed study is needed about the direct conversion of Arabian Light (AL) crude oil, which has a very high production capacity. It is important to examine the possibilities of thermal cracking and catalytic cracking, at different temperature levels and different catalyst to oil ratios and the effect of different catalysts. Moreover, yields of ethylene and propylene need to be enhanced, and conversion of heavy fraction, undesired products, need to be higher.

CHAPTER 3

MATEREIALS AND METHODS

3.1 Background

This chapter provides an overview of feedstocks used in this study. In addition, it gives information about catalyst used and its characterization. Furthermore, the operation of Micro Activity Test (MAT) unit will be discussed. Lastly, principles of instruments used for analyzing products will be discussed.

3.2 Feed

Feedstocks used in this research, AL, AXL, and ASL, where obtained from a domestic oil company. Saudi Arabia has a production capacity of 0.2, 1.2, 8 million barrels per day of ASL, AXL, and AL, respectively, which contributes to nearly 90% of total Saudi capacity [35]. Physical properties of ASL, AXL, and AL are presented in Table 9. Among the three crudes ASL has the lowest sulfur content (0.1 wt.%) followed by AXL (1.3 wt.%), and AL (1.7 wt.%). The API gravity is decreasing in order: ASL > AXL > AL with the corresponding values of: 51º, 39º, and 34º. The naphtha content of ASL is 50 wt.% while for AXL is 38 wt.% and for AL is 35 wt.%. The middle distillates account for 26, 27, and 29 wt.% for AL, AXL, and ASL, respectively. ASL has the highest ratio of 343-°C/343+°C of 3.8. On the other hand, AL has the lowest ratio of 1.5. All three crudes have a paraffinic nature that is confirmed by the K-factor with the following values of 12.6, 12.0, and 11.8, which corresponds to ASL, AXL, and AL, respectively. The PIONA analysis of the naphtha fraction of the crudes is: 46/18/0/9/27 for AL, 34/31/0/8/27 for AXL, and 34/32/0/19/15 for ASL.

Table 9 Properties of Arabian Light crude oil feedstocks [30]

Property	Arabian Light (AL)	Arabian Extra Light (AXL)	Arabian Super Light (ASL)
Sulfur (wt.%)	**1.7**	**1.3**	**0.1**
Density at 15°C, kg/m^3	**892**	**828**	**774**
Gravity, °API	**34**	**39.3**	**51.3**
Vanadium (ppm)	**16**	**2.7**	**1**
Nickel (ppm)	**3.3**	**< 1**	**< 1**
Kin. Viscosity, @ 21 °C (cSt)	**10.2**	**5.8**	**2.3**
Nickel (ppm)	**3.3**	**< 1**	**< 1**
Microcarbon residue (wt.%)	**3.6**	**2.20**	**0.46**
PIONA naphtha fraction (wt.%)	**46/18/0/9/27**	**34/31/0/8/27**	**34/32/0/19/15**
Simulated distillation (°C)			
IBP*	**22**	**25**	**22**
50%	**307**	**287**	**242**
FBP**	**580**	**577**	**558**
Distillation cuts (wt.%)			
Light naphtha (C_5-221°C)	**34**	**38**	**50**
Middle distillates (221-343 °C)	**26**	**27**	**29**
Heavy oil (343°C+)	**39**	**35**	**21**
Elemental analysis (wt.%)			
C	**84.3**	**84.3**	**85.3**
H_2	**12.2**	**12.6**	**14.0**
N_2	**0.64**	**0.70**	**0.53**
UOP K-Factor	**11.76**	**12.0**	**12.55**
Saudi production***	**8**	**1.2**	**0.2**

* Initial boiling point; ** Final boiling point; *** Million barrel per day

3.3 Catalysts

M-cat is a fresh MFI (ZSM-5) zeolite additive supported on a matrix and E-cat is an equilibrium FCC USY catalyst. Both catalysts were procured from a domestic refinery. Prior to cracking experiments, M-cat was steamed in a fixed bed steamer for 6 h at 810 ºC and E-cat was calcined at 650 ºC for 3 h. During calcination, the temperature increase was 5 ºC /min. The activity of M-cat was equilibrated similar to the normal FCC catalyst used in industry.

Physical and chemical properties of E-cat and M-cat are shown in Table 10. Surface area, pore volume, and average pore diameter of E-cat were higher than of M-cat. Pore volume of M-cat was found to be half of E-cat. The surface area for E-cat and M-cat were 157 and 126 m^2/g, respectively. The SiO_2/Al_2O_3 ratio for E-cat was measured as 3.3 and for M-cat was 5.6. Two major desorption peaks were shown in the NH_3-TPD for both catalysts. Those two peaks have a maxima in the low and high temperature regions [30]. The peaks in the low temperature reign (100-300 °C) correspond to the adsorbed ammonia molecules either as Na^+ cations or as NH_4^+ species formed on acidic sites (Brønsted). Moreover, the peaks in the high temperature (300-600 °C) region were assigned to the desorbed ammonia molecules from the acid sites. The acidity profile of M-cat and E-cat is shown in Figure 14. The acidity of the catalysts was studied by NH_3-TPD. As shown in Table 10 the acidity of M-cat was found to be 0.49 mmol/g and the acidity of E-cat was nearly five times lower (0.09 mmol/g), but most of the acidity of M-cat was in the weak to moderate region (below 450 ºC). The strong acidity of E-cat and M-cat was similar. Those differences in properties of catalysts will play a significant role in catalytic cracking of the crude oil.

Table 10 Properties of E-cat and M-cat [2,30,36]

Property	E-cat	M-cat
SiO_2/Al_2O_3 ratio*	3.30	5.61
Pore volume, cc/g	0.19	0.11
Micropore volume, cc/g**	0.062	0.049
Average Pore Diameter (nm)	10.87	7.35
Surface area, m^2/g	157	126
High temperature, 300-600°C	0.02	0.16
Low temperature, 100- 300 °C	0.07	0.33
Total acidity (NH_3-TPD), mmol/g***	0.09	0.49

* Found by ICP analysis; ** Measured by t-plot; *** Determined by ammonia desorption.

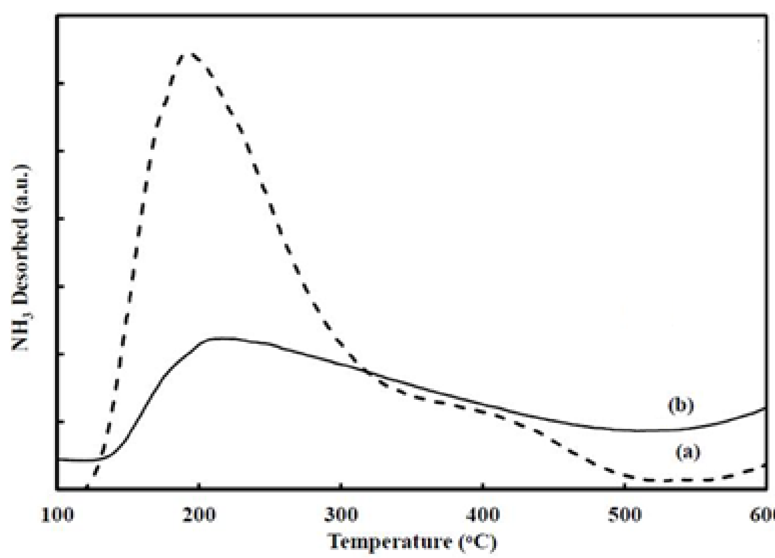

Figure 14 Ammonia temperature programmed desorption profiles for (a) M-cat and (b) E-cat. [36]

Figure 15 present the XRD patterns for the catalysts. In case of M-cat, a peak with high intensity at 21-24° (2 θ) with some other peaks at 6-10° show MFI characteristic peaks. For E-cat, the peak with the highest intensity was at 6.0° that is attributed to the existence of (1,1,1) crystal plane, other peaks at 27.2°, 23.7°, 20.3°, 18.6°, 15.5°, 11.8°, and 10.0°

that are corresponding to (642), (533), (440), (333), (331), (311), and (220) crystal planes, respectively. Those peaks for E-cat show a typical XRD pattern for zeolite of type Y reported in the literature [37].

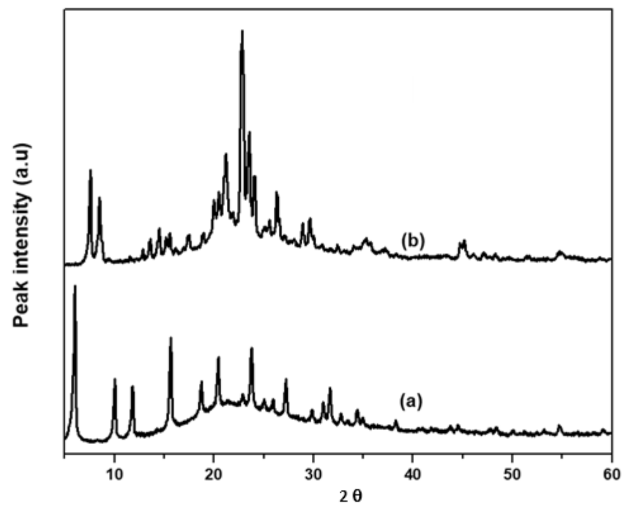

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Figure 15 XRD patterns of (a) E-cat and (b) M-cat [2]

3.4 Cracking Test

A MAT unit was used to investigate thermal and catalytic cracking of AL, AXL, and ASL crude oils. The MAT unit is operated as a fixed bed reactor. The MAT unit was made in Japan by Sakuragi Rikagaku, according to the ASTM D-3907 method. A modification to the feed injector was done to facilitate the injection and to reduce the blockage. All products were sent out from the reactor to a chilled water bath where the liquid product was condensed in the liquid receiver and the gas product was continued to a vessel where it was collected by displacement of water. MAT experiments were conducted at the four temperature levels 550, 575, 600, and 650 °C. Time on stream (TOS) or feed injection time was chosen to be 30 seconds. After the injection, the catalyst was stripped for 9 mins at the reaction temperature by a flow of 30 cc/min of nitrogen. For thermal cracking, a piece of quartz wool was placed inside the reactor to collect the coke. For catalytic cracking, the catalyst to oil ratio was varied from 1 to 6 by fixing the quantity of feed (1.0 g) and varying the amount of catalyst (1-6 g). The results are repeatable with an accuracy of more than 90%.

3.5 Analysis of Cracked Products

The gas product was analysed by an Agilent 3000 A Micro-GC which involves multi-column and multi-channel system that has four thermal conductivity detectors. By one injection, the GC analyses quantitatively all light hydrocarbons (olefins and paraffins) up to C_6, hydrogen and nitrogen. The liquid product was analyzed by Shimadzu GC 2010 Plus equipped with a flame ionization detector and operated the simulated distillation principle (SimDis) according to the ASTM D-2887 method. This analysis gives the results as three different cuts: naphtha (C_5-221 ºC), LCO (Light Cycle Oil 221–343 ºC), and HCO (Heavy Cycle Oil +343 ºC). The coke deposited on the catalyst was quantified by Horiba carbon-sulfur analyzer. Around 1.0 g of the spent catalyst was mixed with 5 g of tungsten, which acts as a promoter for combustion, and was burned in a furnace at high temperature. The produced carbon dioxide in the combustion gas was analyzed by infrared analyzer, and the amount of carbon was measured as percent of the catalyst mass. All the results were gathered to acquire a detailed product yield distribution of the cracking process to evaluate the conversion and selectivities of the catalysts. This allowed calculation of the conversion defined as the combined yield of gases (H_2 and C_1-C_2), LPG (C_3-C_4) and coke.

CHAPTER 4

THERMAL AND CATALYTIC CONVERSION OF ARABIAN LIGHT CRUDE OIL

4.1 Background

This chapter discusses thermal and catalytic cracking of Arabian Light crude oil, which has a density of 34 °API, between 550 °C and 650 °C. Firstly, thermal and catalytic cracking will be compared at the same conversion 34% at 650 °C. Then, effect of temperature for both thermal and catalytic cracking of AL crude oil will be investigated. After that, the effect of C/O ratio on conversion and product yields will also be inspected. Lastly, the effect of mixing catalysts (E-cat and M-cat) at different percentages will be evaluated

4.2 Thermal Versus Catalytic Cracking at Constant Conversion

Thermal and catalytic cracking of AL crude oil was investigated at 650 °C and compared at the same conversion. The differences between catalytic and thermal cracking are compared in terms of products yields, which are LPG, light olefins, dry gas, coke, naphtha, LCO, and HCO.

For thermal cracking, conversion is function of temperature and contact time. For catalytic cracking, conversion is not only function of temperature and contact time, it is also function other factors, such as, catalyst to oil ratio (C/O) and type of catalyst. So, the experimental results for catalytic cracking, for both catalysts, were interpolated to get the same conversion as thermal cracking to have comparative results. A C/O of 0.94 was needed for E-cat to achieve the same conversion as thermal cracking. However, due to the higher activity of M-cat, only 0.48 C/O was needed to achieve the same conversion.

Table 11 shows the products yields for thermal and catalytic cracking of AL crude oil at 650 °C at the same conversion of 34%. At the same conversion, the LPG (C_3–C_4) yield for thermal cracking was 17.1 wt.%., whereas E-cat enhanced the LPG yield to 18.4 wt.%. and M-cat further increased the yield of LPG to 19.7 wt.%. LPG is produced by cracking of the naphtha-range reactive species of the AL crude oil [2,30]. The propane yield increased in the order thermal cracking (0.93 wt.%) < E-cat (1.16 wt.%) < and M-cat (1.28 wt.%). On the other hand, butanes (normal butane and iso-butane) yield for E-cat was the highest among M-cat and thermal cracking results.

From Table 11 total yield of light olefins (C_2–C_4) was 22.8 wt.% for thermal cracking case, whereas catalytic cracking led to 22.5 wt.% and 24.7 wt.% over E-cat and M-cat, respectively.

Ethylene yield decreased in the following order: thermal > M-cat > E-cat. Thermal cracking produced ethylene by the beta-session of primary radicals which results in free radicals that undergo further beta-scission. This leads to ethylene. In catalytic cracking, ethylene is not favored, since its formation would involve primary intermediate carbenium ions that are relatively unstable [24]. Instead, branching isomerization reactions lead to carbenium ions that undergo beta-session to propyl carbenium ions that deprotonate to afford propylene. The maximum yield of propylene was for M-cat with 10.8 wt.%. Thermal and E-cat gave the same yield. C_4 butenes yield was the highest for E-cat with 7.5 wt.%, whereas M-cat and thermal showed a similar yield. The decrease in C_4 butenes for M-cat and thermal is caused by the further cracking of C_4 butenes to form ethylene and propylene.

Dry gas yield for thermal cracking was higher than for catalytic cracking (15.8 wt.% for thermal, 14.6 wt.% for E-cat, and 14.5 wt.% for M-cat). Yield of dry gas for thermal cracking was increased due to the further cracking of light olefins. Coke yield increased in order M-cat < thermal < E-cat. E-cat yield of coke was 1.5 wt.%

E-cat resulted in the highest naphtha yield (37.4 wt.%), followed by thermal cracking (34.4 wt.%), and M-cat (31.4 wt.%). The yield of LCO increased in the order M-cat < thermal < E-cat (for M-cat was 17.6 wt.%, for E-cat 17.3 wt.%, and 16.4 wt.%). As shown in Table 11 a similar trend was observed for HCO.

Table 11 Products yields for thermal and catalytic cracking of AL crude oil at 650 °C and 34% conversion.

Catalyst	Thermal	E-cat	M-cat
CAT/OIL	-	0.94	0.48
Mass balance	90.8	90.6	90.5
Yields (wt.%)			
H_2	0.2	0.2	0.1
C_1	4.6	4.5	3.9
C_2	3.4	3.4	3.1
C_2=	7.6	6.5	7.3
H_2-C_2 (dry gas)	15.8	14.6	14.5
C_3	0.9	1.2	1.3
C_3=	8.6	8.5	10.8
iC_4	0.2	0.3	0.2

nC_4	0.7	0.9	0.8
C_4=	6.7	7.5	6.6
C_3-C_4 (LPG)	17.1	18.4	19.7
C_2=-C_4=	22.8	22.5	24.7
C_2=-C_3=	16.2	15.0	18.1
C_3=+C_4=	15.3	16.0	17.4
Total gas	32.8	32.9	34.2
Naphtha (Feed = 34.6%)	34.4	37.4	31.4
LCO (Feed = 26.1%)	17.3	16.4	17.6
HCO (Feed = 39.3%)	14.7	11.8	16.6
Coke	0.8	1.5	0.2
CMR[1]	103.4	44.1	77.0
HTC[2]	-	0.2	0.2
P/E[3]	1.1	1.3	1.5
Ratios (mol/mol)			
C_2=/C_2	2.4	2.1	2.5
C_3=/C_3	9.7	7.7	8.8
C_4=/C_4	8.0	6.6	6.7
iC_4=/C_4=	0.2	0.3	0.3
iC_4=/iC_4	9.8	5.9	10.7

[1] CMR = (dry gas/iC4)
[2] HTC = $(nC_4 + iC_4)/C_4^{=}$
[3] P/E = $C_3^{=}/C_2^{=}$

4.3 Effect of Temperature

Thermal and catalytic cracking of AL crude oil was studied at four different temperatures (550, 575, 600, 650 °C) and constant C/O ratio of 4 over the two catalysts (E-cat and M-cat). Results are evaluated in terms of conversion (produced gas and coke) and yields of light olefins, LPG, dry gas, naphtha, HCO, LCO and coke. Conversion and products yield are shown in Table 12 for temperatures of 550 and 650 °C. The performance of catalytic cracking was compared via some yield ratios, such as CMR (Cracking Mechanism Ratio) that is defined as the ratio of dry gas produced to isobutane yield, and HTC (Hydrogen Transfer Coefficient), which is the ratio in yields of butanes to butenes, and P/E (propylene yield to ethylene yield). [21–23,38,39]

Table 12 Yield of products for thermal and catalytic cracking of AL crude oil at 550 and 650°C, C/O of 4.

Temperature (°C)	550	650	550	650	550	650
Catalyst	Thermal cracking		E-cat		M-cat	
CAT/OIL	-	-	3.74	3.85	3.75	3.75
Conversion	6.5	33.6	26.0	50.0	29.8	49.1
Mass balance	94.6	90.8	92.5	91.8	92.7	90.8
Yields (wt.%)						
H_2	0.0	0.2	0.1	0.4	0.1	0.3
C_1	0.7	4.6	1.4	6.1	1.1	4.2
C_2	0.7	3.4	1.3	4.3	1.6	4.2
C_2=	1.1	7.6	1.9	7.6	3.8	10.9
H_2-C_2 (dry gas)	2.5	15.8	4.7	18.4	6.6	19.6
C_3	0.3	0.9	1.2	1.9	6.9	4.0
C_3=	1.2	8.6	6.2	12.5	7.0	15.7
iC_4	0.1	0.2	2.8	0.9	1.9	0.7
nC_4	0.7	0.7	1.4	1.1	2.6	1.4
C_4=	1.5	6.7	7.0	10.3	4.3	6.0

C_3-C_4 (LPG)	3.9	17.1	18.7	26.7	22.6	27.8
C_2=-C_4=	3.8	22.8	15.1	30.3	15.0	32.7
C_2=-C_3=	2.3	16.2	8.1	20.0	10.8	26.6
C_3=+C_4=	2.7	15.3	13.2	22.7	11.2	21.7
Total gas	6.4	32.8	23.4	45.1	29.2	47.4
Naphtha (Feed = 34.6%)	34.9	34.4	48.3	32.5	24.4	21.5
LCO (Feed = 26.1%)	24.6	17.3	17.9	11.1	16.2	15.6
HCO (Feed = 39.3%)	34.0	14.7	7.8	6.4	29.6	14.4
Coke	0.1	0.8	2.6	4.9	0.6	1.7
CMR	21.7	103.4	1.7	19.4	3.4	29.7
HTC	0.6	0.1	0.6	0.2	1.1	0.3
P/E	1.1	1.1	3.3	1.6	1.8	1.4
Ratios (mol/mol)						
C_2=/C_2	1.6	2.4	1.6	1.9	2.6	2.8
C_3=/C_3	3.7	9.7	5.2	6.8	1.1	4.1
C_4=/C_4	1.9	8.0	1.7	5.2	1.0	3.1
iC_4=/C_4=	0.2	0.2	0.3	0.3	0.4	0.4
iC_4=/iC_4	2.0	9.8	0.7	3.2	0.9	3.2

Figure 16 presents conversion as function of temperature for thermal cracking and catalytic cracking (E-cat and M-cat). In general, as temperature increases, conversion increases.

At low temperature (550 °C), conversion for thermal cracking was lower than for catalytic cracking. E-cat enhanced the conversion from 6.5 wt.% up to 26.0 wt.%. Furthermore, M-cat increased the conversion up to 29.8 wt.%. Catalytic cracking has more activity towards cracking than thermal cracking.

At high temperature (650 °C) the same trend was observed with conversions 33.6 wt.%, 50.0 wt.%, and 49.1 wt.% for thermal, E-cat, and M-cat, respectively. The increase in conversion over M-cat is caused by the further cracking of HCO due to the high temperature, for example, HCO yield decreased from 29.6 down to 14.4 wt.%. The cracking of HCO increased naphtha content which further cracked to produce light olefins which contribute to conversion. The increase in conversion for thermal cracking is mainly due to the increase in dry gas yield.

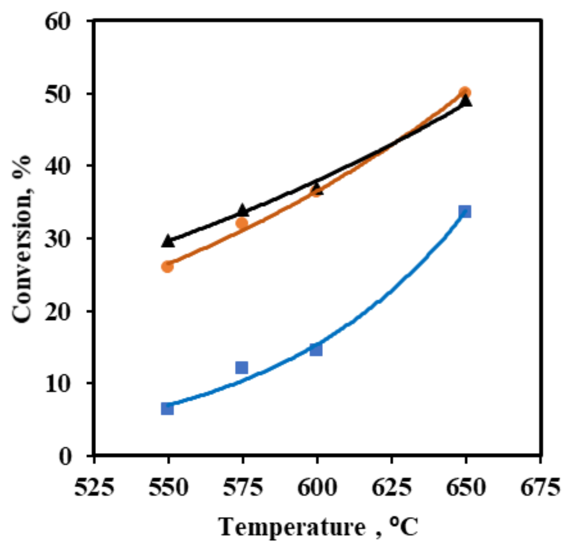

Figure 16 Temperature effect on conversion of AL crude oil cracking (■) Thermal, (●) E-cat, and (▲) M-cat.

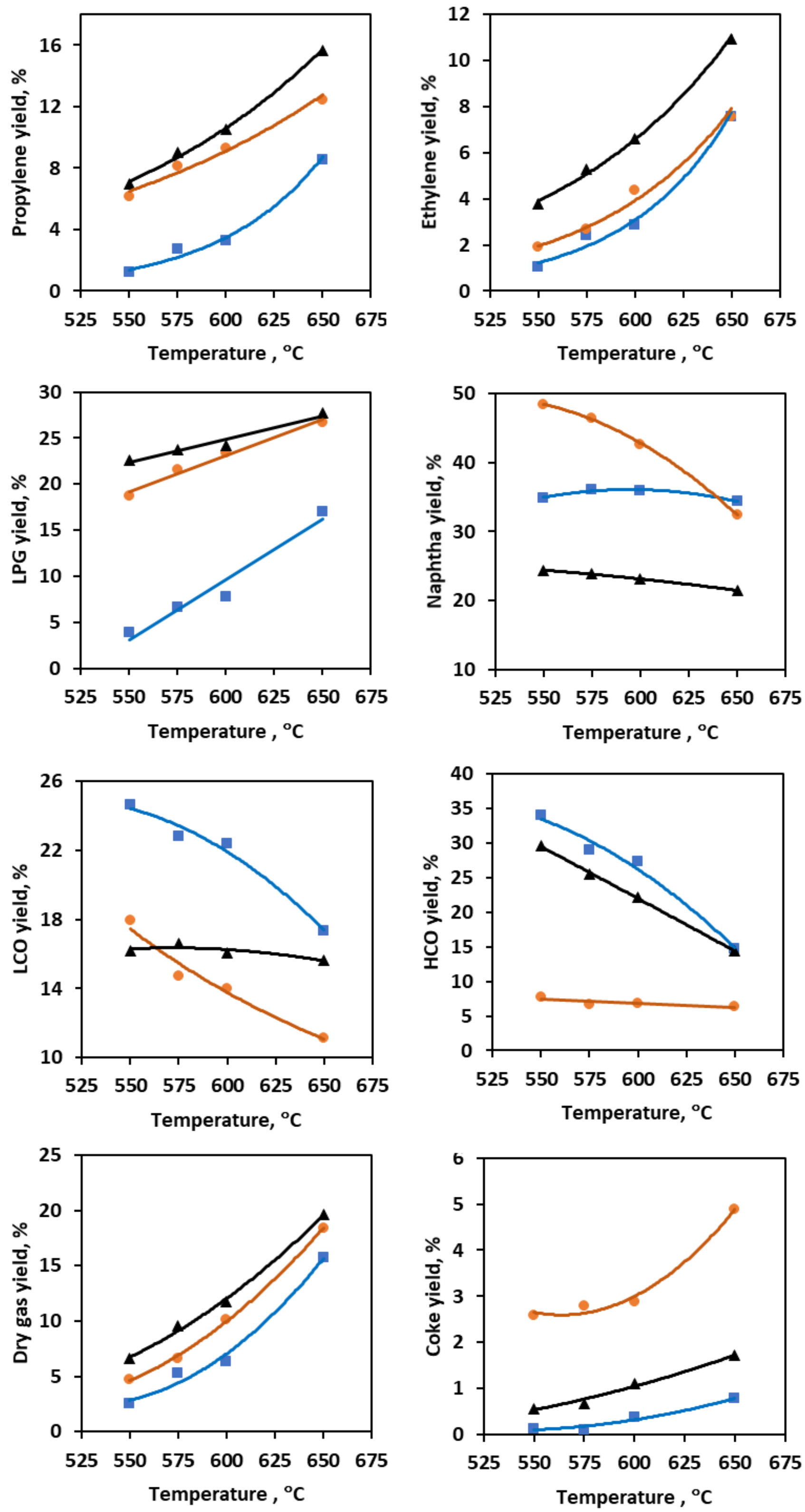

Figure 17 Temperature effect on product yields of AL crude oil cracking (■) Thermal, (●) E-cat, and (▲) M-cat.

4.3.1 LPG Yield

As shown in Table 12 and Figure 17 a linear relationship was observed between temperature and the yield of LPG (C_3–C_4) for both thermal and catalytic cracking. In the reaction temperature range M-cat showed the highest yield that started from 22.6 wt.% at 550 °C up to 27.8 wt.% at 650 °C. LPG yield over E-cat was slightly less than M-cat at 650 °C with a yield of 27.7 wt.%. However, at 550 °C the difference between M-cat and E-cat increased with a yield over E-cat of 18.7 wt.%. On the other hand, the yield of LPG via thermal cracking was the lowest. Even at the maximum temperature 650 °C, the yield of LPG was lower than the yield of catalytic cracking at 550 °C. The yield of LPG was 3.9 wt.% at 550 °C and increased up to 17 wt.% at 650 °C. The enhancement in the yield of LPG is attributed to the hydrogen transfer ratio that reflects bimolecular reactions and hydrogen transfer activity. In the hydrogen transfer (HT) reaction, two olefins or olefin and naphthene are reacted to form aromatic and paraffin through intermediates by transfer of hydrogen. The chain stops since aromatics are very stable. HT reactions increase naphtha yield. Olefins are the reactive species in naphtha for secondary reactions that produce LPG; therefore, the decrease in hydrogen transfer reactions indirectly increase "over-cracking" of the naphtha. [22,39] All values of hydrogen transfer coefficient (HTC) decreased for all cases. For example, for E-cat it decreased from 0.6 at 550 °C to 0.2 at 650 °C, which indicates decrease in butanes yield and increase in the yield of $C_4^{=}$ olefins.

Propane yield over M-cat showed a decrease by increasing temperature. For example, at 550 ºC the propane yield was 6.9, at 600 ºC was 5.2, and at 650 ºC was 4.0 wt.%. The reason for the decrease in propane may be accredited to the small pore size of M-cat which further cracks propane at high temperature to produce lower hydrocarbons. For example, the yield of methane increased from 1.1 at 550 ºC up-to 4.2 at 650 ºC. On other hand, increasing temperature in cracking over E-cat increased propane yield.

The temperature effect on yields of LPG olefins and paraffins is plotted in Figure 18. For catalytic cracking, the yield of LPG paraffins decreased as the temperature increased. M-cat resulted in the highest yields of paraffinic LPG at all temperatures starting from 11.4 wt.% at 550 °C to 6 wt.% at 650 °C. Thermal cracking showed a small net increase of 0.6 wt.% in the LPG paraffins yield between 550 °C and 650 °C. On the other hand, the yield of LPG olefins increased for both thermal and catalytic cracking. E-cat gave the highest yield of LPG olefins, the yield increased from 13.2 wt.% up to 22.7 wt.%. M-cat showed the same trend and the gap between M-cat and E-cat at 650 °C was only 1 wt.%. For all cases, the olefinicity of LPG (LPG olefins/LPG paraffins) increased with the increase in temperature. For instance, for thermal cracking it increased from 2.3 at 550 °C to 8.5 at 650 °C.

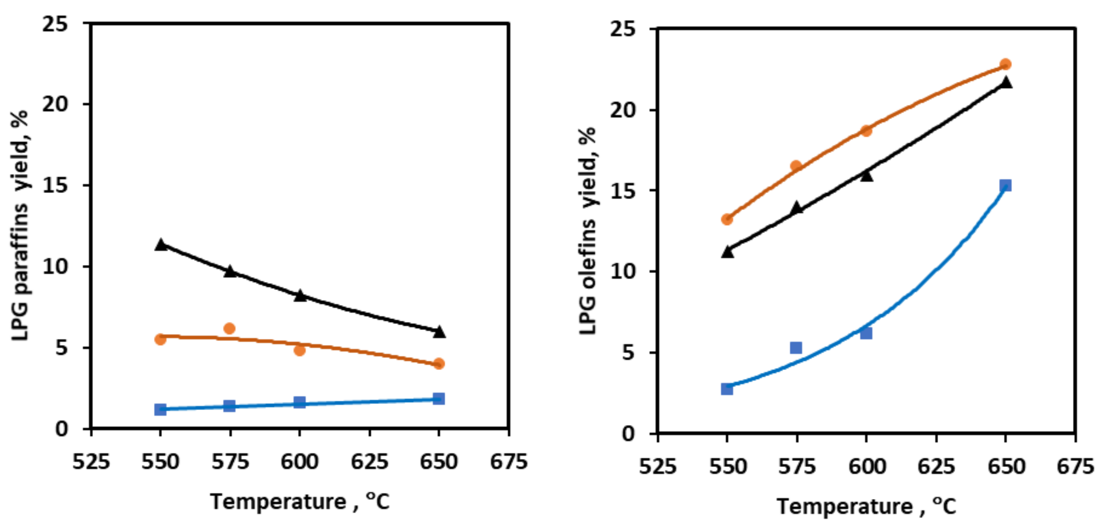

Figure 18 Temperature effect on LPG olefins and LPG paraffins yields of AL crude oil cracking (■) Thermal, (●) E-cat, and (▲) M-cat

4.3.2 Light Olefins Yields

As illustrated in Figure 19 the overall yield of light olefins (C_2–C_4) showed an increase with increasing temperature for both thermal and catalytic cracking. Thermal cracking showed lower yield compared to catalytic cracking. The yield for thermal cracking increased from 3.8 wt.% at 550 °C up to 22.9 wt.% at 650 °C. Both M-cat and E-cat resulted in a similar overall yield of light olefins below 600 °C. Above 600 °C, M-cat showed a minor superiority over E-cat. At 550 °C, the yield of light olefins was 15.1 wt.% and 15 wt.% for E-cat and M-cat receptively, at 650 °C, the yields were 30.3 wt.% and 32.7 wt.%, receptively. The increment in light olefins yield is caused by the conversion of naphtha-range reactive species. [23,40,41] For instance, as shown in Figure 20 when the temperature was increased from 550 °C to 650 °C, there was a decrease in the naphtha yield over E-cat from 48.3 wt.% to 32.5 wt.% associated with an enhancement of light olefins yield from 15.1 wt.% to 30.3 wt.%.

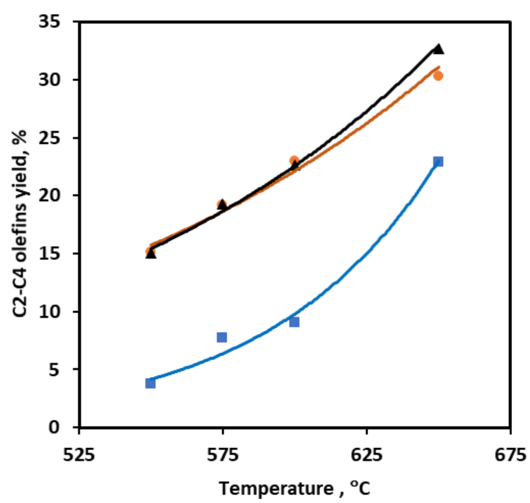

Figure 19 Temperature effect on light olefins yield for the cracking of AL crude oil over (■) Thermal, (●) E-cat, and (▲) M-cat.

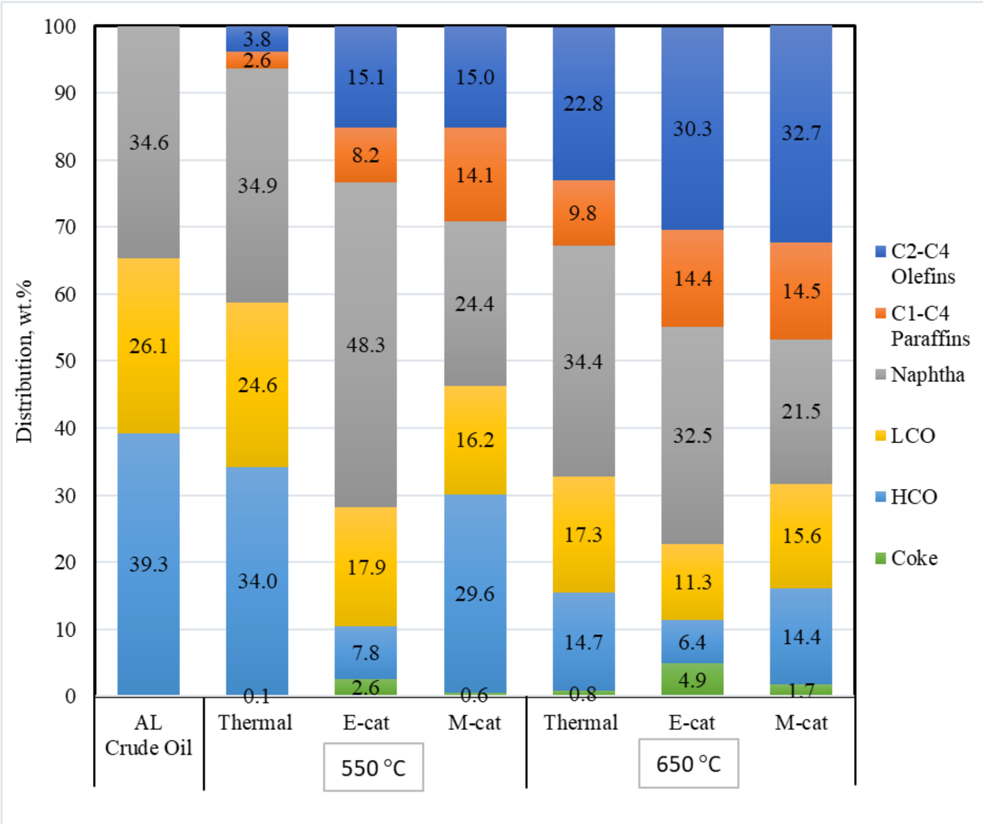

Figure 20 Temperature effect on products distribution of AL crude oil cracking.

In all cases, total yield of ethylene and propylene increased by increasing temperature, and the yield order was M-cat > E-cat > thermal. Propylene yield for catalytic cracking was higher than thermal cracking due to the carbenium ion mechanism for beta-session which favors propylene. The maximum yields of ethylene and propylene were 10.9 wt.% and 15.7 wt.%, respectively, achieved over M-cat. The increase in ethylene yield of M-cat in comparison to E-cat may be attributed to the higher acidity of M-cat than E-cat. Another reason for the increase in ethylene yield can be attributed to the smaller pore size of M-cat which mainly target cracking the naphtha fraction in the feed while larger molecules, such as LCO and HCO cannot access those pores which is not the case for E-cat. The ratio of propylene to ethylene (P/E) decreased as temperature increased for all cases. The increase in ethylene yield resulted by the contribution of thermal cracking which agrees with literature[42–44] . The contribution of propylene to light olefins decreased in order M-cat (48%) > E-cat (41%) > thermal (38%). Form Table 12 the total yield of C_4 olefins was achieved over E-cat with a maximum of 10.3 wt.% at 650 °C and 30% of C_4 olefins was contributed by isobutene.

4.3.3 Naphtha Yield

From Table 9 and Figure 20, the amount of naphtha (C_5-221°C) in AL crude oil was 34.6 wt.%. The naphtha cut of AL crude oil contains mainly paraffins (64 wt.%), followed by aromatics (27%), and naphthenes (9%). As shown in Figure 17, thermal cracking and E-cat generally resulted in an increase in naphtha content compared with the feed, except for 650 °C, where the naphtha product was less than 2 wt.% compared to the feed. The increase is attributed to two main reasons: the produced naphtha from LCO and HCO and the unreacted naphtha available in the feed[28]. In general, as the temperature increases, the yield of naphtha decreases. This decrease is associated with an increase in the yield of light olefins. Between 550 °C and 650 °C, E-cat resulted in the largest drop in naphtha yield (15.9 wt.%), followed by M-cat (2.9 wt.%), and lastly thermal cracking (0.5 wt.%). The highest yield of naphtha at 550 °C was at 48.3 wt.% over E-cat. At 650 °C, thermal cracking gave the highest naphtha yield at 34.4 wt.%. The reason for yielding high naphtha over E-cat is explained by the nature of the catalyst which cracks HCO and LCO and transforms them into molecules in the range of naphtha. M-cat cannot crack these oil cuts due to its pore size and simply converts the molecules in the naphtha range into mainly LPG and gases. Accordingly, the naphtha obtained on M-cat has a higher octane number, as it has a higher aromatic content than that obtained on E-cat (it cracks the paraffin compounds in the naphtha range and the alkyl groups in the aromatic compounds in the naphtha range).

Therefore, a naphtha with more aromatic compounds and less paraffinic ones than on E-cat is obtained.

4.3.4 LCO and HCO Yields

The temperature effect on the yields of LCO and HCO is shown in Table 12 and illustrated in Figure 17. LCO and HCO are the heavy ends which are cracked to lighter components. As shown in Figure 17, all yields of LCO and HCO decreased as the temperature increased for both thermal cracking and catalytic cracking. LCO and HCO account for 26.1 wt.% and 39.3 wt.% of the AL feed. Thermal cracking showed the least conversion for LCO at HCO between 550 °C and 650 °C. At 650 °C, LCO and HCO yields were 17.3 wt.% and 14.7 wt.%, respectively. M-cat yield of HCO yield decreased linearly as temperature increased. However, the yield of LCO was nearly constant (the change between 550 °C and 650 °C was 0.6 wt.%) which indicates that: 1) an equivalent amount of the cracked HCO is further cracked from the LCO to lighter products or, 2) HCO is directly cracked to lighter products, or 3) combination of both. E-cat showed the smallest yields of LCO and HCO over the whole range of temperatures. At 650 °C, the yields were 11.1 wt.% and 6.4 wt.% for LCO and HCO, respectively. The ability of E-cat compared with M-cat to crack the heavy parts is mainly explained by the larger pores of the E-cat than M-cat.

4.3.5 Dry Gas and Coke Yields

As shown in Figure 17, the yield of dry gas (hydrogen, methane, ethane, and ethylene) for both thermal and catalytic cracking increased sharply by increasing the temperature. At all temperatures, M-cat gave the highest yields of dry gas followed by E-cat and then thermal cracking. The increase of dry gas for catalytic cracking was lower than for thermal cracking. Even M-cat resulted in the highest yield of dry gas at all temperatures such as 19.6 wt.% at 650 °C. The increase between 550 °C and 650 °C was the lowest. Dry gas yield for E-cat increased from 4.7 wt.% at 550 °C up to 18.4 wt.% at 550 °C. For thermal cracking, the yield of dry gas increased from 2.5 wt.% at 550 °C up to 15.8 wt.% at 650 °C.

The cracking mechanism ratio (CMR) is ratio of dry gas to isobutane. This is plotted versus temperature in Figure 21 so that the variations of dry gas yield can be compared. M-cat showed a higher CMR than E-cat at all temperatures. For example, at 550 °C CMR was 1.7 and 3.4 for E-cat and M-cat, respectively. By increasing the reaction temperature, CMR ratio increased to 19.4 and 29.7 for E-cat and M-cat, respectively. The higher CMR for M-cat is explained by contribution of protolytic cracking in comparison to the beta scission cracking and carbenium ion mechanisms over E-cat that includes bimolecular reactions such as intermolecular hydrogen transfer [22,39]. M-cat showed a higher yield of ethylene in comparison to E-cat, which may be attributed to the medium pore size of M-cat. This is caused by larger interaction between the reactants and catalytic surface of the catalyst and resulted in a higher conversion of linear olefins toward ethylene. The low yield of isobutane and high yield of ethylene resulted from the highly activated free radical chain reaction [22,39]. The CMR for thermal cracking was higher than catalytic cracking. In addition, there was a dramatic increase in CMR above 575 °C.

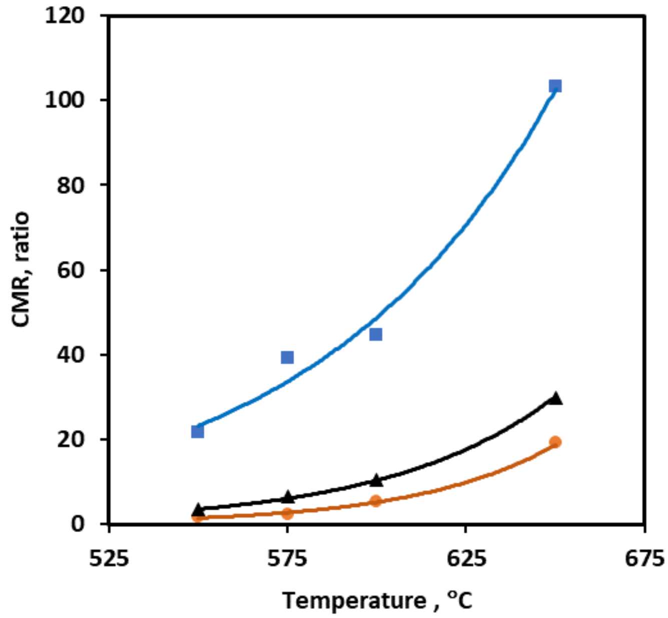

Figure 21 Temperature effect on CMR (Cracking Mechanism Ratio) of AL crude oil cracking (■) Thermal, (●) E-cat, and (▲) M-cat.

Coke can be formed via many pathways. Important reactions are di- and poly-alkenes, cyclization of alkynes, followed by aromatization and condensation. By these reactions, poly-aromatic compounds are formed, which are referred to as coke[8]. The coke is deposited on the catalyst and causes deactivation. As shown in Figure 17, the yield of coke was the highest over E-cat at all temperatures. It increased with the increase in temperature reaching a maximum of 4.9 wt.% at 650 °C, which agrees with literature[9,11,29,30]. M-cat showed a lower coke yield than E-cat (1.7 wt.% at 650 °C). Thermal cracking resulted in the lowest coke yield.

4.4 Effect of Catalyst to Oil (C/O) Ratio

The effect of C/O ratio for catalytic cracking of AL crude oil was investigated for both catalysts, at a constant temperature of 650 °C by varying the C/O ratio from 1 to 6.

For both catalysts the conversion of the AL crude oil was plotted against C/O ratio, as shown in Figure 22. In general, as the C/O ratio increased the conversion of the AL crude oil increased. A nearly linear relationship between C/O ratio and conversion appeared in the range 1 to 3 C/O ratio after that as the C/O ratio increased, the increase in conversion was marginal, and this is a typical behaviour for cracking in MAT unit which is explained by the higher influence on the conversion at lower severe conditions of the experiment [40]. At low C/O ratios, M-cat is more active due to its shape selectivity and acidity, and so may crack the naphtha fraction of the oil to give LPG and dry gas. For example, at a C/O ratio of 1 the conversion achieved over M-cat was 39% compared to 33% over E-cat. Nevertheless, high C/O ratios, i.e., more severe conditions, E-cat has a better performance for cracking the heavier fractions, HCO and LCO, which is not the case for M-cat due to its shape selectivity. Under these conditions of high C/O ratios, E-cat cracks the heavy fraction, forming a small amount of LPG and dry gas and, furthermore, cracks the naphtha fraction. Accordingly, a higher conversion than that on M-cat is obtained.

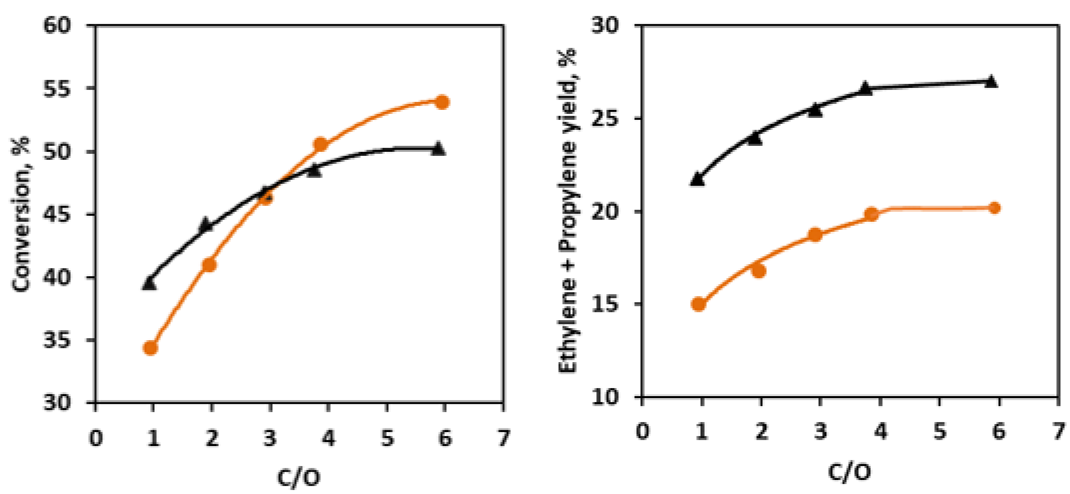

Figure 22 Effect of C/O ratio on conversion and ethylene and propylene yield of AL crude oil catalytic cracking over (●) E-cat, and (▲) M-cat.

As shown in Table 13 all yields of ethylene, propylene, LPG, dry gas, and coke increased by increasing the C/O ratio for both E-cat and M-cat. On the other hand, the naphtha yield decreased by the increase in C/O ratio due to the cracking of naphtha range components to light olefins. The ethylene + propylene yield was plotted versus C/O ratio in Figure 22. Below C/O of 4 there was a proportional relationship between C/O ratio and yield of ethylene + propylene. The further increment of C/O ratio had a minor effect on the yield. The highest yield of ethylene + propylene achieved over E-cat was 20.2 wt.% at C/O of 6 and for M-cat, at the same condition, the yield was 27.0 wt.%.

Table 13 Catalyst to Oil (C/O) ratio effect on product yields for AL crude oil catalytic cracking at 650°C, over E-cat, and M-cat.

Catalyst	E-cat					M-cat				
CAT/OIL	0.94	1.96	2.91	3.85	5.94	0.92	1.89	2.90	3.75	5.88
Conversion	34.4	41.0	46.3	50.0	53.9	39.6	44.2	46.7	49.1	50.2
Mass balance	90.6	90.4	90.8	91.8	93.0	92.7	94.2	94.0	90.8	92.7
Yields (wt.%)										
H_2	0.2	0.3	0.3	0.4	0.5	0.2	0.2	0.2	0.3	0.2
C_1	4.5	4.8	5.2	6.1	5.5	3.8	4.0	4.6	4.2	4.6
C_2	3.4	3.6	3.7	4.3	3.9	3.1	3.6	3.8	4.2	3.8
C_2=	6.5	6.7	6.9	7.6	7.2	8.1	9.6	10.3	10.9	10.3
H_2-C_2 (dry gas)	14.6	15.4	16.1	18.4	17.1	15.1	17.4	18.9	19.6	18.9
C_3	1.2	1.3	1.6	1.9	2.5	1.7	3.3	2.6	4.0	2.7
C_3=	8.5	10.1	11.9	12.5	12.9	13.7	14.3	15.2	15.7	16.7
iC_4	0.3	0.5	1.0	0.9	2.1	0.3	0.5	0.4	0.7	0.4
nC_4	0.9	0.9	1.1	1.1	1.5	1.0	1.3	1.2	1.4	1.2

$C_4=$	7.5	9.2	10.5	10.3	7.5	7.3	6.6	7.5	6.0	7.7
C_3-C_4 (LPG)	18.4	22.1	26.1	26.7	29.1	23.9	26.1	26.9	27.8	28.7
$C_2=$-$C_4=$	22.5	26.1	29.3	30.3	30.2	29.0	30.6	33.0	32.7	34.7
$C_2=$-$C_3=$	15.0	16.8	18.8	20.0	20.2	21.8	23.9	25.5	26.6	27.0
$C_3=+C_4=$	16.0	19.3	22.4	22.7	23.0	20.9	21.0	22.7	21.7	24.4
Total gas	32.9	37.5	42.2	45.1	46.3	39.1	43.5	45.8	47.4	47.6
Naphtha (Feed = 34.6%)	37.4	37.3	35.0	32.5	31.2	26.8	23.4	22.8	21.5	23.3
LCO (Feed = 26.1%)	16.4	13.8	12.0	11.1	9.8	16.1	15.8	15.3	15.6	14.3
HCO (Feed = 39.3%)	11.8	7.9	6.8	6.4	5.1	17.4	16.7	15.2	14.4	12.2
Coke	1.5	3.5	4.0	4.9	7.7	0.6	0.7	0.9	1.7	2.6
CMR	44.1	30.5	16.8	19.4	8.0	57.7	34.4	47.9	29.7	48.3
HTC	0.2	0.2	0.2	0.2	0.4	0.2	0.3	0.2	0.3	0.2
P/E	1.3	1.5	1.7	1.6	1.8	1.7	1.5	1.5	1.4	1.6
Ratios (mol/mol)										
$C_2=/C_2$	2.1	2.0	2.0	1.9	2.0	2.8	2.8	2.9	2.8	2.9
$C_3=/C_3$	7.7	7.9	7.5	6.8	5.3	8.4	4.5	6.2	4.1	6.4
$C_4=/C_4$	6.6	6.7	5.2	5.2	2.9	5.9	3.9	4.9	3.1	5.1
$iC_4=/C_4=$	0.3	0.3	0.3	0.3	0.3	0.4	0.4	0.4	0.4	0.4
$iC_4=/iC_4$	5.9	5.2	3.3	3.2	1.5	9.8	4.7	6.8	3.2	7.1

M-cat showed a superiority over E-cat in all yields except for naphtha and coke. The lower naphtha yield for M-cat is due to the diffusion limitations of the catalyst which results in the favourably of cracking of naphtha-range components in comparison to E-cat which cracks heavier parts and produces more naphtha[1]. Furthermore, the higher yields of coke over E-cat compared to M-cat is attributed to the larger pores of E-cat which target cracking larger molecules that result in high amounts of coke.

4.5 Effect of Mixing Catalysts

Catalytic cracking of AL crude oil was also investigated by mixing both the E-cat and M-cat catalysts in varying proportions at a temperature of 650 ºC and a constant C/O ratio of 6. Table 14 presents the experimental results. The two limits of the experiment are 0% M-cat, which corresponds to 100% E-cat, and 100% M-cat. At 0% M-cat the yield of ethylene + propylene was 20.2 wt.% and the yield of naphtha was 31.2 wt.%, whereas at 100% M-cat, the yields of ethylene + propylene and naphtha were 27.0 and 23.3 wt.%., respectively. M-cat was added to E-cat at different percentages to enhance the yields of light olefins. Figure 23 shows the effect of addition of M-cat on the yields of light olefins, naphtha, and LPG. A contradictory relationship between the yields of ethylene + propylene versus naphtha is noticed that is explained earlier by the cracking of naphtha components to produce light olefins. In addition, the amount of ethylene + propylene + naphtha is nearly constant along the x-axis (different proportions of M-cat) with a yield of 52.1 ±1.7 wt.%.

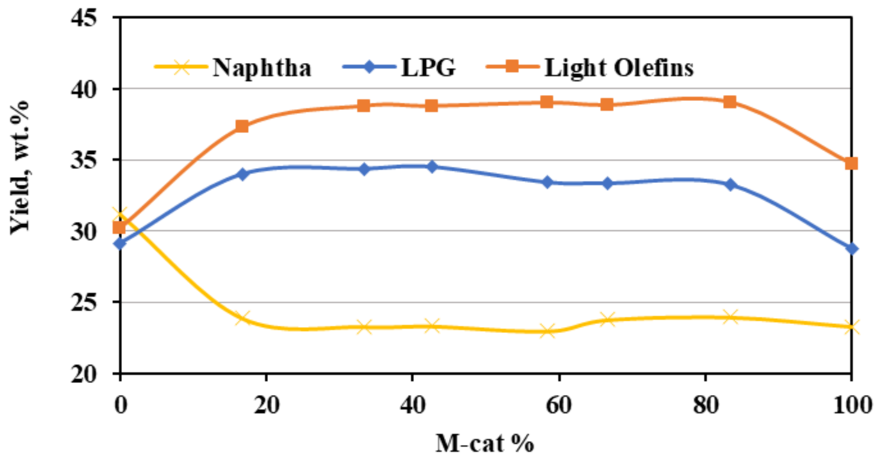

Figure 23 Effect of M-cat addition to E-cat on yields of naphtha, LPG and light olefins of AL crude oil catalytic cracking at C/O of 6.0 and temperature of 650 °C.

Table 14 Effect of mixing catalysts on yield of products for AL crude oil catalytic cracking at 650°C and C/O of 6.

M-cat %	0	17	33	43	58	67	83	100
Conversion	53.9	61.1	60.7	60.9	60.0	58.0	56.1	50.2
Mass balance	93.0	92.9	93.0	90.5	92.6	93.2	91.2	92.4
Yields (wt.%)								
H_2	0.5	0.5	0.4	0.4	0.3	0.3	0.3	0.2
C_1	5.5	5.9	5.7	5.5	5.6	5.2	4.8	4.6
C_2	3.9	4.2	4.1	4.1	4.3	3.9	3.8	3.8
C_2=	7.2	9.2	9.9	10.1	10.7	10.4	10.5	10.3
H_2-C_2 (dry gas)	17.1	19.8	20.0	20.1	20.9	19.8	19.5	18.9
C_3	2.5	3.0	2.9	3.2	2.9	2.9	2.8	2.7
C_3=	12.9	18.4	19.2	19.3	19.2	19.2	19.3	16.7
iC_4	2.1	1.6	1.3	1.3	0.9	0.7	0.6	0.4
nC_4	1.5	1.3	1.3	1.3	1.3	1.2	1.3	1.2
C_4=	10.1	9.6	9.7	9.4	9.2	9.3	9.2	7.7
C_3-C_4 (LPG)	29.1	34.0	34.4	34.5	33.4	33.3	33.2	28.7

C_2=-C_4=	30.2	37.3	38.8	38.8	39.0	38.9	39.1	34.7
C_2=-C_3=	20.2	27.7	29.1	29.4	29.8	29.6	29.8	27.0
C_3=+C_4=	23.0	28.1	28.9	28.7	28.4	28.5	28.5	24.4
Total gas	46.3	53.8	54.4	54.6	54.4	53.2	52.7	47.6
Naphtha (Feed = 34.6%)	31.2	23.9	23.3	23.3	23.0	23.8	24.0	23.3
LCO (Feed = 26.1%)	9.8	9.8	10.2	10.1	10.8	11.7	12.6	14.3
HCO (Feed = 39.3%)	5.1	5.2	5.8	5.7	6.2	6.5	7.3	12.2
Coke	7.7	7.3	6.3	6.3	5.6	4.8	3.4	2.6
CMR	8.0	12.6	15.8	15.5	22.3	26.8	33.2	48.3
HTC	0.4	0.3	0.3	0.3	0.2	0.2	0.2	0.2
P/E	1.8	2.0	1.9	1.9	1.8	1.9	1.8	1.6
Ratios (mol/mol)								
C_2=/C_2	2.0	2.4	2.6	2.6	2.7	2.8	2.9	2.9
C_3=/C_3	5.3	6.4	6.9	6.3	7.0	7.0	7.1	6.4
C_4=/C_4	2.9	3.4	4.0	3.7	4.3	4.8	5.2	5.1
iC_4=/C_4=	0.3	0.4	0.4	0.4	0.4	0.4	0.4	0.4
iC_4=/iC_4	1.5	2.2	2.7	2.6	3.5	4.5	5.6	7.1

Even though the yields of light olefins from 30% M-cat up to 83% M-cat was nearly constant there was an optimum yield of ethylene + propylene achieved at 58% M-cat with a yield of 29.8 wt.%. In detail the yields of ethylene and propylene were 10.7 and 19.2 wt.%, respectively. The yield of naphtha at this optimum point was 23.0 wt.%. Due to the higher cost of M-cat compared to E-cat, 30% M-cat is considered a better choice since the yield of ethylene and propylene is still high (29 wt.%) with a naphtha yield of 23 wt.%.

The yields of heavy parts LCO and HCO increased from 14.8 wt.% at 0% M-cat up to 26.4 wt.% at 100%M-cat, due to the less amount of E-cat available to crack the heavy ends. On the other hand, the coke yield showed a decrease by increasing the M-cat, from 7.7 wt.% at 0% M-cat down to 2.6 wt.% at 100% M-cat.

In summary, the main parameters that play a major role in the direct conversion of crude oil and products distribution are: temperature, catalyst to oil ratio, catalyst pore size, and percentage of mixing catalysts. The increase in temperature for both thermal and catalytic cracking resulted in an enhancement in yields of light olefins, LPG, dry gas, and coke associated with a decrease of naphtha, LCO, and HCO. The increment in C/O ratio showed a similar trend to the increase in temperature in terms of increases and decreases in yields. Catalysts with large pores will enhance the naphtha and coke yields associated with high decrease in LCO and HCO yields. On the other hand, catalysts with small pores will increase the yields of light olefins and decrease the yield of naphtha. Lastly, light olefins yields can be boosted by mixing catalysts of different pore sizes.

CHAPTER 5

COMPARISION BETWEEN THERMAL AND CATALYTIC CRACKING OF DEFFERENT ARABIAN LIGHT CRUDE OILS

5.1 Background

This chapter discusses thermal and catalytic cracking of three kinds of light crude oils namely Super Light (ASL), Extra Light (AXL) and Arabian Light (AL), which have API gravities of 51 º, 39 º, and 34º, respectively, between 600 º C and 650 º C. First of all, thermal cracking of the three crude oils will be investigated. After that, the effect of different catalysts and their mixture will be studied at a constant conversion of 50% and temperature of 650 ºC. Lastly, the effect of catalyst to oil (C/O) ratio over the optimum catalyst for all crude oils will be inspected at two temperatures (600 and 650 ºC).

5.2 Thermal Cracking

Thermal cracking of the three crude oils ASL, AXL, and AL was studied at three different temperatures (600, 625, and 650 ºC). Conversion is a strong function of temperature (severity of the process) and as shown in Figure 24 for all crudes the relationship between temperature and conversion is highly linear. From Table 15 at 600 ºC, all crude oils resulted in nearly similar conversion, 14.2 wt.% for AL, 14.0 wt.% for AXL, and 14.5 wt.% for ASL. Above 600 ºC, ASL and AXL had the same conversion, whereas AL crude oil resulted in a higher conversion. For example, at 650 ºC the corresponding conversions for ASL, AXL, and AL were: 27.6, 27.0, and 32.8 wt.%, respectively.

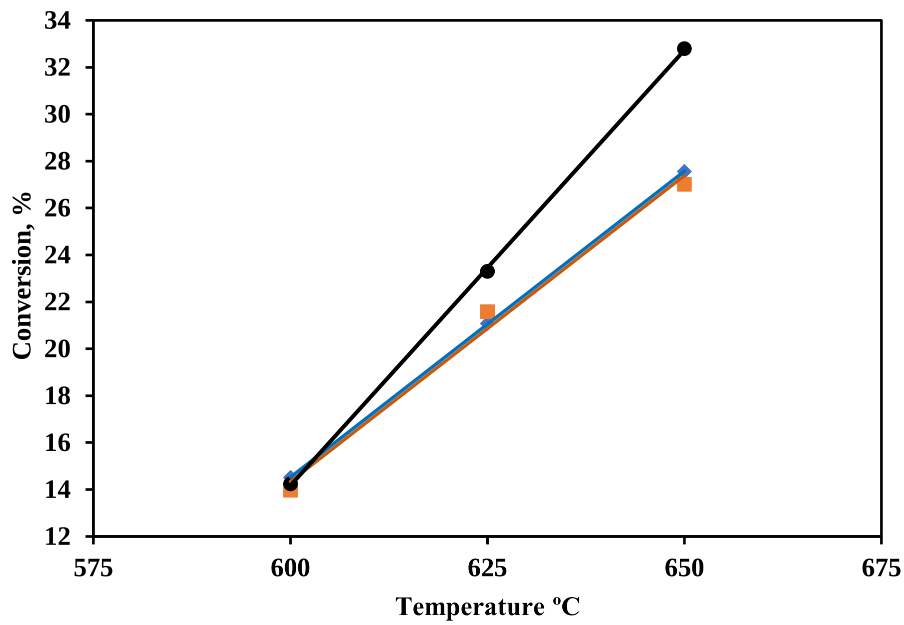

Figure 24 Effect of temperature on conversion for thermal cracking of (●) AL, (■) AXL, and (♦) ASL crude oils.

Table 15 Products yields for thermal cracking of ASL, AXL, and AL crude oils, at 600, 625, and 650 ºC.

Temperature (ºC)	600	625	650	600	625	650	600	625	650
Feed		**ASL**			**AXL**			**AL**	
Mass balance	95.4	95.8	96.0	95.7	92.6	92.9	94.2	91.6	90.8
Conversion (%)	14.5	21.1	27.6	14.0	21.6	27.0	14.2	23.3	32.8
Yields (wt.%)									
H_2	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2
C_1	1.5	2.5	3.6	1.7	2.8	3.5	1.8	3.1	4.6
C_2	1.2	1.9	2.3	1.5	2.3	2.8	1.6	2.5	3.4
$C_2^=$	**2.6**	**4.1**	**6.1**	**3.1**	**5.0**	**6.5**	**2.8**	**5.1**	**7.6**

C_3	0.4	0.5	0.6	0.4	0.6	0.6	0.6	0.7	0.9
$C_3^=$	**3.1**	**5.0**	**6.8**	**3.4**	**5.5**	**6.9**	**3.2**	**5.7**	**8.6**
iC_4	0.5	0.5	0.5	0.0	0.1	0.1	0.1	0.1	0.2
nC_4	1.4	1.4	1.3	0.3	0.3	0.3	0.7	0.7	0.7
Total Gas	14.3	20.8	27.2	13.7	21.2	26.5	13.9	22.7	32.8
Naphtha	**48.7**	**52.7**	**48.0**	**40.8**	**41.6**	**38.1**	**36.5**	**38.5**	**34.4**
LCO	23.5	17.6	16.9	22.8	19.3	19.2	22.1	18.8	17.3
HCO	13.3	8.6	7.5	22.4	17.4	15.7	27.2	19.4	14.7
Coke	0.2	0.3	0.4	0.3	0.4	0.5	0.4	0.6	0.8
$C_2^= + C_3^=$	**5.7**	**9.1**	**12.8**	**6.5**	**10.5**	**13.5**	**6.1**	**10.8**	**16.2**
H_2-C_2 (dry gas)	5.4	8.6	12.1	6.4	10.2	13.0	6.3	10.8	15.8
C_3-C_4 (LPG)	8.9	12.2	15.1	7.3	11.0	13.5	7.6	12.0	17.1
$C_2^=$-$C_4^=$	**9.2**	**14.0**	**18.8**	**9.7**	**15.2**	**19.0**	**9.1**	**15.6**	**22.8**
$C_4^=$	3.4	4.9	6.0	3.2	4.6	5.6	3.0	4.7	6.7
CMR*	11.0	18.4	26.8	141.9	172.1	182.6	57.4	95.0	103.4
P/E**	1.2	1.2	1.1	1.1	1.1	1.1	1.1	1.1	1.1
C_1-C_4	5.1	6.7	8.2	4.0	6.0	7.4	4.7	7.0	9.8
LPG olefins	6.6	9.8	12.8	6.5	10.1	12.5	6.2	10.5	15.3
LPG paraffins	2.3	2.4	2.3	0.7	0.9	1.0	1.4	1.5	1.8
LPG olefinicity	2.8	4.1	5.5	8.8	11.1	12.6	4.6	7.1	8.5
Ratios (mol/mol)									
$C_2^=/C_2$	2.3	2.4	2.8	2.2	2.4	2.5	1.9	2.2	2.4
$C_3^=/C_3$	7.8	10.0	12.7	8.3	10.2	11.3	6.1	8.4	9.7
$C_4^=/C_4$	1.9	2.7	3.5	10.3	13.9	16.4	3.9	6.4	8.0
$iC_4^=/C_4^=$	0.2	0.2	0.3	0.2	0.2	0.2	0.2	0.2	0.2
$iC_4^=/iC_4$	1.5	2.5	3.3	13.8	16.8	17.3	5.5	9.1	9.8

* CMR = (dry gas/iC_4)

** P/E = $C_3^=$/ $C_2^=$

5.2.1 LPG and Light Olefins Yields

LPG (C_3-C_4) is mainly produced from the cracking of the reactive compound of the crude that are in the naphtha-range hydrocarbons [45]. As shown in Figure 25, the yields of LPG, ethylene, and propylene have a highly linear relationship with temperature. The behavior of yield of LPG for ASL and AXL versus temperature was similar and at all temperature levels ASL resulted in a higher yield of LPG. For instance, at 650 ºC the LPG yields were 15.1 and 13.5 wt.% for ASL and AXL, respectively. On the other hand, AL crude oil exhibited a higher slop than ASL and AXL. At low temperature (600 ºC), the LPG yield was 7.6 wt.%. At 650 ºC the yield sharply increased, in comparison to ASL and AXL, to 17.1 wt.%. The LPG olefinicity (LPG olefins/ LPG paraffins) for all crudes increased with increasing temperature. Furthermore, as shown in Table 15 AXL crude oil showed the highest LPG olefinicity at all temperature levels.

From Table 15 the yields of ethylene at 600 ºC increased in order: ASL (2.6 wt.%) < AL (2.8 wt.%) < AXL (3.1 wt.%). However, as the temperature increased to 650 ºC the order of crudes changed to the succeeding order: ASL (6.1 wt.%) < AXL (6.5 wt.%) < AL (7.6 wt.%). Ethylene is formed due the free radical and beta-session mechanisms. In more details, due to the high temperature, by the cleavage of carbon-carbon bond uncharged molecules "free radicals" with an unpaired of electron are formed. Those free radicals are very reactive. They undergo beta-session to produce ethylene and primary free radical. The primary free radical will further undergo beta-session to produce more ethylene [29].

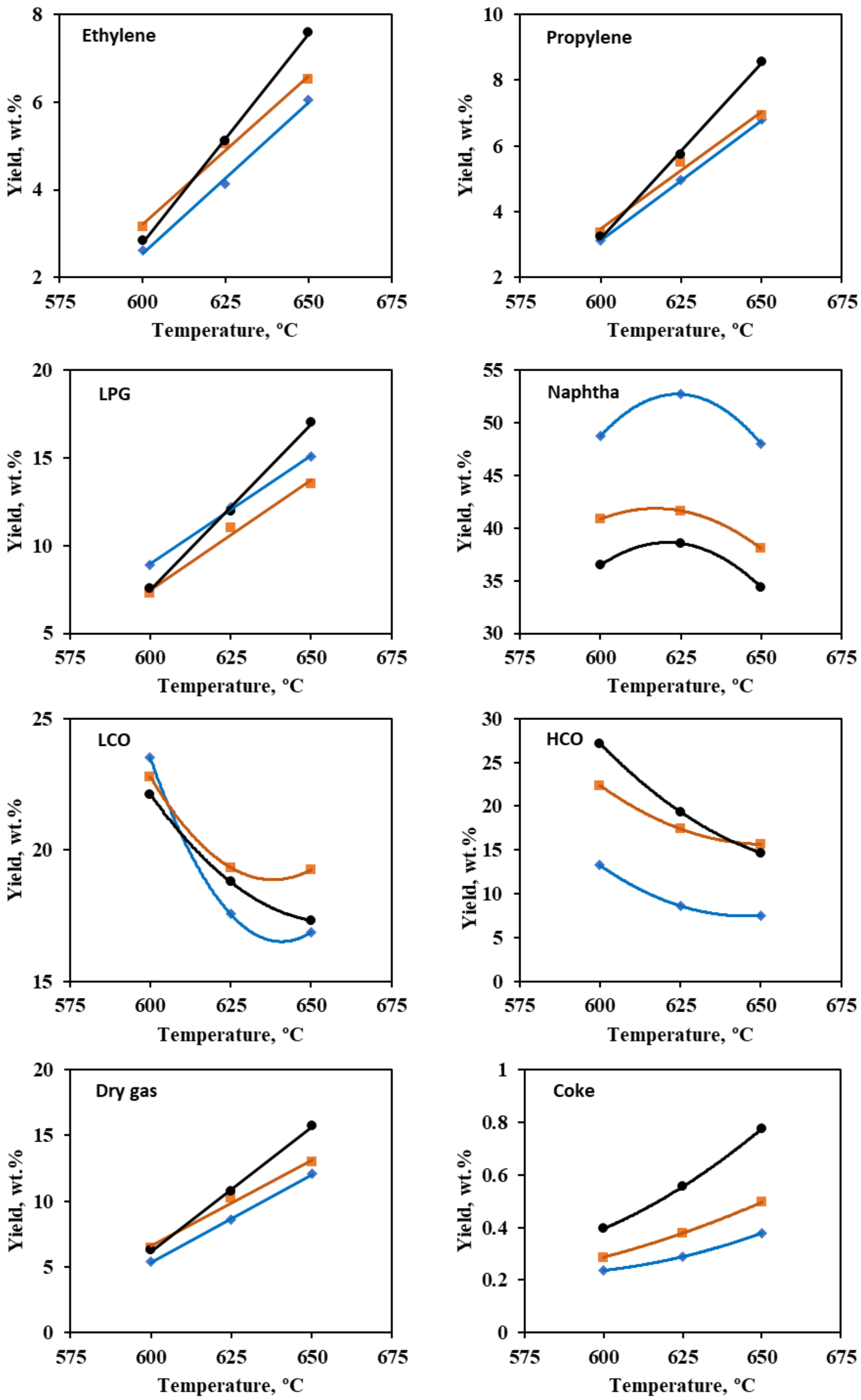

Figure 25 Effect of temperature on product yields for thermal cracking of (●) AL, (■) AXL, and (♦) ASL crude oils.

Propylene yields showed a similar trend to ethylene. The highest yield of propylene was achieved form the cracking of AL crude oil at 650 ºC (8.6 wt.%) followed by almost a similar yield of ASL (6.8 wt.%) and AXL (6.9 wt.%). The yield of butenes showed an increase with temperature with a trend similar to LPG yield against temperature. In all cases, butene-1 has the highest yield of butenes ranged from 30 to 40% of total butenes.

The molar yields of ethylene/ethane (C_2=/C_2) and propylene/propane (C_3=/C_3) are shown in Table 15. For both molar ratios for all crude oils as the temperature increases, the selectivity towards olefins in comparison to paraffins increases. ASL crude oil showed the highest ratios of C_2=/C_2 and C_3=/C_3, for example, at 650 ºC the C_2=/C_2 and C_3=/C_3 were 2.8 and 12.7, respectively. On the other hand, AL showed the lowest ratios, for instance, at 650 ºC the C_2=/C_2 ratio was 2.4 and the C_3=/C_3 ratio was 9.7. In addition, the ratio of propylene/ethylene (P/E) is almost constant with a value of 1.1.

5.2.2 Naphtha, LCO and HCO Yields

From Table 9 the amount of naphtha that is present in ASL, AXL, and AL are 50, 38, 34 wt.%, respectively. The yields on naphtha for all crudes are shown in Table 15 and plotted in Figure 25. For all crudes naphtha yields increased to reach a maximum at 625 ºC, then it dropped. This behavior is explained since naphtha is considered as a reactant that cracks to form light hydrocarbons and as product that is formed from the cracking of heavier cuts that are available in the feed. At all range of temperatures, the yield of naphtha for ASL was the highest and for AL was the lowest due to the amount of naphtha that is already available in the crude oil. For example, at 650 ºC yields of naphtha for ASL, AXL, and AL were 48, 38.1, and 34.4 wt.%, respectively.

ASL crude oil has the largest amount of LCO (29 wt.%), followed by AXL (27 wt.%), then AL comes last with 26 wt.% as shown in Table 9. Figure 25 shows how LCO yields decrease with increasing temperature. From 600 ºC to 625 ºC, the drop in LCO was very sharp. After 625 ºC, the LCO yield was less steep for AL and nearly flat for ASL and AXL. The decrease in LCO yields is associated with an enhancement in yields of naphtha and light olefins. The largest drop in LCO compared to the feed was observed for thermal cracking of ASL crude oil which was from 29 to 16.9 wt.% at 650 ºC.

The percent of HCO present in crude oils: AL, AXL, and ASL as stated in Table 9 are: 39, 35, and 21 wt.%, respectively. For all crude oils, as shown in Figure 25 the amount of HCO left in the liquid product decreased with the further rise in temperature because of the further cracking of heavy cuts into lighter hydrocarbons and coke at higher temperature. ASL crude oil resulted in the lowest yield of HCO since the quantity that is already available in the feed is the lowest among all feeds. The unconverted HCO in the products at 650 ºC were 14.7 wt.% for AL, 15.7 wt.% for AXL, and 7.5 wt.% for ASL. Figure 26 demonstrates product distribution for thermal cracking for all crude oils at 650 ºC in comparison to the feed.

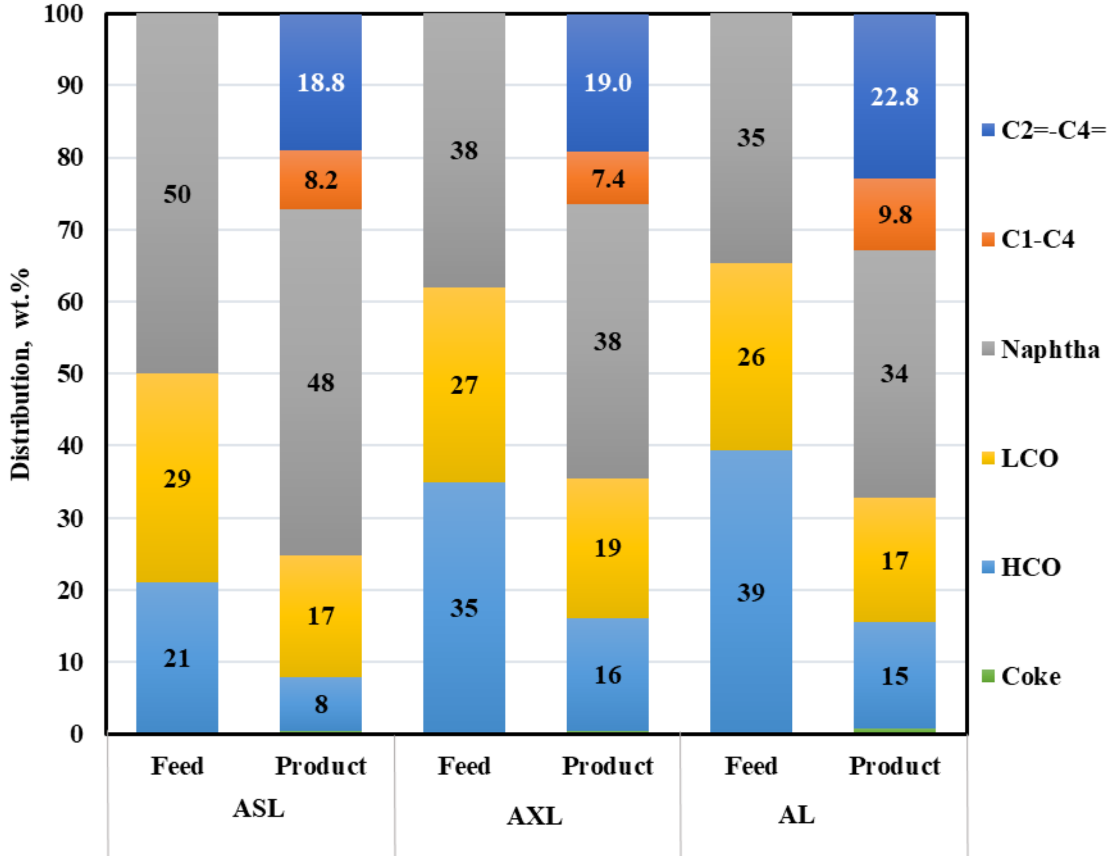

Figure 26 Products yield distribution for thermal cracking of AL, AXL, and ASL crude oils compared to feeds at 650 ºC.

5.2.3 Dry Gas and Coke Yields

For the three crudes, the yields of dry gas (H_2, C_1-C_2) maintained the highly linear relationship against temperature as illustrated in Figure 25 with AL having the largest amount of dry gas at all temperatures. For example, the maximum yield of dry gas was 15.8 wt.% which was produced from AL crude oil at 650 ºC. As shown in Table 15 for all experiments almost 50% of the dry gas in ethylene. Methane yield also increased by the further increase in temperature. Methane is produced by free radicals and alpha-session mechanisms. The methyl radical is produced by the alpha-session. This radical extract a hydrogen atom for any adjacent hydrocarbon which produce methane and another free radical. Alpha-session occurred even though it is not thermodynamically favored compared to beta-session. That's way the yield of ethylene is much higher than the yield of methane.

The CMR (cracking mechanism ratio) is the yield of dry gas divided by the yield of isobutane. The CMR increased by increasing temperature for all crude oils. For instance, the CMR for AL crude oil at 600, 625 and 650 ºC were, 57.4, 95.0, and 103.4, respectively (Table 15). The increase in CMR over the increase in temperature indicates the influence of protolytic cracking compared to beta-session and carbenium ion mechanisms [22].

Coke is produced because of the over-cracking of heavy hydrocarbons. As the percentage of heavy cuts increases, type of crude, or the severity (temperature) of the process increases the possibly of producing more coke increases which is illustrated in Figure 25. AL crude oil which contains a high amount of HCO compared to AXL and ASL resulted in more coke, followed by AXL, and finally come the lightest feed that is ASL crude oil.

5.3 Comparison Between Catalysts at the Same Conversion

Catalytic cracking of AL, AXL, and ASL crude oils was investigated at the same conversion at 650 ºC by three catalysts, E-cat, M-cat, and a mixture of 30% M-cat and 70% E-cat. Experimental data were interpolated to get a 50% conversion for the sake of comparison. Products distribution of catalytic cracking of the crude oils is shown in Table 16.

For all crude oils the cracking over M-cat /E-cat, by with lower catalyst to oil ratio (C/O) compared to E-cat and M-cat separately, resulted in the same conversion (50%). For example, for AXL crude oil the C/O ratio required to accomplish 50% conversion was 6.04, 5.73, and 2.82 over E-cat, M-cat, and M-cat /E-cat, respectively.

Table 16 Comparative data for catalytic cracking of ASL, AXL, and AL crude oils, at 50% conversion, over E-cat, M-cat and M-cat/E-cat, at 650 °C.

Temperature (°C)	650			650			650		
Catalyst	E-cat	M-cat/E-cat	M-cat	E-cat	M-cat/E-cat	M-cat	E-cat	M-cat/E-cat	M-cat
Feed	**ASL**			**AXL**			**AL**		
Mass balance	96.7	96.6	96.6	94.2	93.9	94.5	91.8	91.2	92.4
C/O	5.95	3.14	6.04	6.04	2.82	5.73	3.85	2.02	5.88
Yields (wt.%)									
H_2	0.4	0.2	0.3	0.4	0.2	0.3	0.4	0.2	0.2
C_1	4.3	3.9	4.1	5.4	3.9	4.4	6.0	4.3	4.6
C_2	2.6	2.8	3.4	3.7	3.1	3.9	4.3	3.2	3.8
$C_2^=$	**5.4**	**8.6**	**10.5**	**6.9**	**8.9**	**11.1**	**7.5**	**8.4**	**10.3**
C_3	2.2	2.0	3.3	2.2	2.1	3.4	1.9	1.9	2.7
$C_3^=$	**14.9**	**17.7**	**17.2**	**14.1**	**18.5**	**16.9**	**12.3**	**17.4**	**16.7**
iC_4	3.9	1.3	0.8	2.1	0.7	0.5	0.9	0.5	0.4
nC_4	2.3	1.9	2.0	1.0	0.8	1.0	1.1	1.1	1.2
Total Gas	47.7	48.5	49.7	46.7	48.5	49.0	44.7	46.8	47.6
Naphtha	**41.8**	**38.8**	**35.5**	**36.3**	**31.0**	**25.7**	**32.1**	**27.5**	**23.3**
LCO	6.6	9.5	10.5	8.3	12.3	13.5	11.0	14.9	14.3
HCO	1.9	2.1	3.6	4.1	6.3	10.3	6.3	8.6	12.2
Coke	2.0	1.0	0.7	4.5	2.0	1.5	5.9	2.2	2.6
$C_2^= + C_3^=$	**20.3**	**26.3**	**27.7**	**21.0**	**27.4**	**28.1**	**19.8**	**25.8**	**27.0**
H_2-C_2 (dry gas)	12.7	15.5	18.2	16.3	16.1	19.7	18.2	16.1	18.9
C_3-C_4 (LPG)	34.9	33.0	31.4	30.4	32.4	29.3	26.5	30.7	28.7
$C_2^=$-$C_4^=$	**31.9**	**36.5**	**35.8**	**31.9**	**37.6**	**35.6**	**30.0**	**35.6**	**34.7**

$C_4^=$	26.5	27.9	25.3	25.1	28.7	24.5	22.5	27.2	24.4
HTC*	0.5	0.3	0.3	0.3	0.2	0.2	0.2	0.2	0.2
CMR**	3.3	12.3	22.9	7.7	21.9	43.6	19.4	30.4	48.3
P/E***	2.7	2.1	1.6	2.1	2.1	1.5	1.6	2.1	1.6
C_1-C_4	15.3	11.8	13.6	14.4	10.7	13.2	14.3	11.0	12.7
LPG olefins	26.5	27.9	25.3	25.1	28.7	24.5	22.5	27.2	24.4
LPG paraffins	8.4	5.1	6.1	5.3	3.7	4.9	4.0	3.5	4.3
LPG olefinicity	3.1	5.5	4.1	4.7	7.7	5.0	5.7	7.8	5.7
Ratios (mol/mol)									
$C_2^=/C_2$	2.2	3.3	3.3	2.0	3.1	3.1	1.9	2.8	2.9
$C_3^=/C_3$	7.1	10.1	5.4	6.8	9.7	5.2	6.8	9.8	6.4
$C_4^=/C_4$	1.9	3.5	3.0	3.6	7.3	5.2	5.2	6.2	5.1
$iC_4^=/C_4^=$	0.3	0.4	0.4	0.3	0.4	0.4	0.3	0.4	0.4
$iC_4^=/iC_4$	0.9	3.2	3.6	1.6	5.8	6.0	3.2	6.7	7.1

* HTC = $(nC_4 + iC_4)/C_4^=$
** CMR = (dry gas/iC_4)
*** P/E = $C_3^=/ C_2^=$

5.3.1 LPG and Light Olefins Yields

The LPG yields for ASL crude oil increased in order: M-cat (31.4 wt.%) < M-cat/E-cat (33.0 wt.%) < E-cat (34.9 wt.%), as shown in Table 16. On the other hand, the order was different for AXL crude oil catalytic cracking, M-cat (29.3 wt.%) < E-cat (30.4 wt.%) < M-cat/E-cat (32.4 wt.%), also for the cracking of AL crude oil with the following order: E-cat (26.5 wt.%) < M-cat (28.7 wt.%) < M-cat /E-cat (30.7 wt.%). The differences in order between the different crudes may be attributed to the different composition of each crude oil and the amount of naphtha-range reactive species that is available in the feed. For all crude oils, the LPG olefinicity showed a similar trend for the three catalysts with the following order E-cat < M-cat < M-cat/E-cat.

As shown in Table 16, ethylene yields for the three crude oils followed the same order over the catalyst with cracking over E-cat resulted in the lowest yield of ethylene, whereas M-cat yielded the largest amount. For example, ASL crude oil catalytic cracking produced 5.4 wt.% of ethylene over E-cat, 8.6 wt.% over M-cat/E-cat, and 10.5 wt.% over M-cat. The difference in the yield of ethylene over E-cat and M-cat may be linked to the medium size of pores of the catalysts. M-cat catalyst has smaller pores which lead to the further cracking of linear olefins to produce more ethylene in comparison to E-cat, which is evidenced in the lower yield of butenes. In catalytic cracking, ethylene is not favored, since its formation contains primary intermediate carbenium ions that are relatively unstable. Instead, branching isomerization reactions lead to carbenium ions that undergo beta-session to propyl carbenium ions that deprotonate to afford propylene [4].

As shown in Table 16 the enhancement in propylene yield is associated with reduction in naphtha yield. Catalytic cracking for AL, AXL, and ASL crude oils over M-cat/E-cat led to the maximum yield of propylene followed by M-cat and E-cat. For example, the yield of propylene for AXL crude oil catalytic cracking was 14.1 wt.% over E-cat, 16.9 wt.% over M-cat, and 18.5 wt.% over M-cat/E-cat. E-cat, due to the larger pores, mainly cracks LCO and HCO which yields more naphtha. However, because of the smaller pores of M-cat which lead to diffusion limitations, targets cracking naphtha-range hydrocarbons to produce more light olefins. So, the combination between E-cat and M-cat lead to increasing light olefins yield, mainly propylene, since E-cat will increase the naphtha yield that will be further cracked to light olefins over M-cat. Another reason for the higher yield of propylene over M-cat compared to E-cat might be credited to the suppression of hydrogen transfer reactions which produce paraffins from olefins [46]. It known that the as the pore of the catalyst gets smaller, the greater the suppression of hydrogen transfer reactions. Bulky bimolecular reaction intermediates cannot be accommodated by the small pores of M-cat. So, catalysts which contains M-cat with narrower pore structures have high shape selectivity towards propylene production [23,46,47].

Furthermore, for all crude oils cracking over M-cat/E-cat showed a higher selectivity of propylene to propane (C_3=/C_3) compared to each catalyst separately. From Table 16, the ratio of C_3=/C_3 for AL, AXL, and ASL crude oils was 9.8, 9.7 and 10.1, respectively.

5.3.2 Naphtha, LCO and HCO Yields

Regardless of the catalyst used, the yield of naphtha increased in order AL, AXL, and ASL due to the initial amount on naphtha that is contained in the feed. For instance, the cracking of AL, AXL, and ASL crude oils over E-cat produced 32.1, 36.3, and 41.8 wt.%, respectively. In comparison, M-cat resulted in a lower yield of naphtha, such as 23.3 wt.% for AL, 25.7 wt.% for AXL, and 35.5 wt.% for ASL. As stated earlier, the reason for the differences in yields over E-cat compared to M-cat are attributed to the nature of each catalyst and its pore size. Clearly as shown in Table 16 cracking over M-cat/E-cat showed some intermediate results between E-cat and M-cat as pure catalysts.

The yields of HCO and LCO showed the same performance for the three crude oils and over the three catalysts. Being the lightest feed, ASL crude oil showed the lowest yields of HCO and LCO over the three catalysts. In contrast, AL crude oil resulted in the highest yields of HCO and LCO. For the same reason that was already mentioned, cracking over

E-cat resulted in the lowest yields of LCO and HCO for all cases, followed by M-cat/E-cat and then pure M-cat. As observed in Table 16 the minimum yields of LCO (6.6 wt.%) and HCO (1.9 wt.%) were accomplished over E-cat for ASL crude oil cracking.

5.3.3 Dry Gas and Coke Yields

As presented in Table 16 almost half the yield of dry gas is contributed from ethylene. Since M-cat produced the highest yields of ethylene for the three crude oils, it resulted in higher amount of dry gas compared to E-cat and M-cat/E-cat. For instance, the yields of dry gas over M-cat for ASL, AL, and AXL crude oils were: 18.2, 18.5, and 18.9 wt.% respectively.

As shown in Table 16, catalytic cracking over E-cat resulted in the highest yields of coke for all crudes. In addition, as the crude get heavier, the coke yield increased. For illustration, the yields of coke over E-cat for AL, AXL, and ASL crude oils were: 5.9, 4.5, and 2.0 wt.%. M-cat produced less amounts of coke, 2.2 wt.% for AL, 1.5 wt.% for AXL, and 0.7 wt.% for ASL, which agrees with literature [18,19]. Since M-cat/E-cat is a mixture of both catalysts, it resulted in-between values of coke.

5.4 Effect of Catalyst to Oil (C/O) Ratio

The C/O ratio effect was investigated for all three crude oils, ASL, AXL, and AL, at 600 and 650 ºC over M-cat/E-cat by varying the C/O from 2 to 6. Figure 27 shows C/O ratio effect on conversion. Figure 28 in addition to Tables 17 and 18 present the products yield distribution of the cracking of the crude oils.

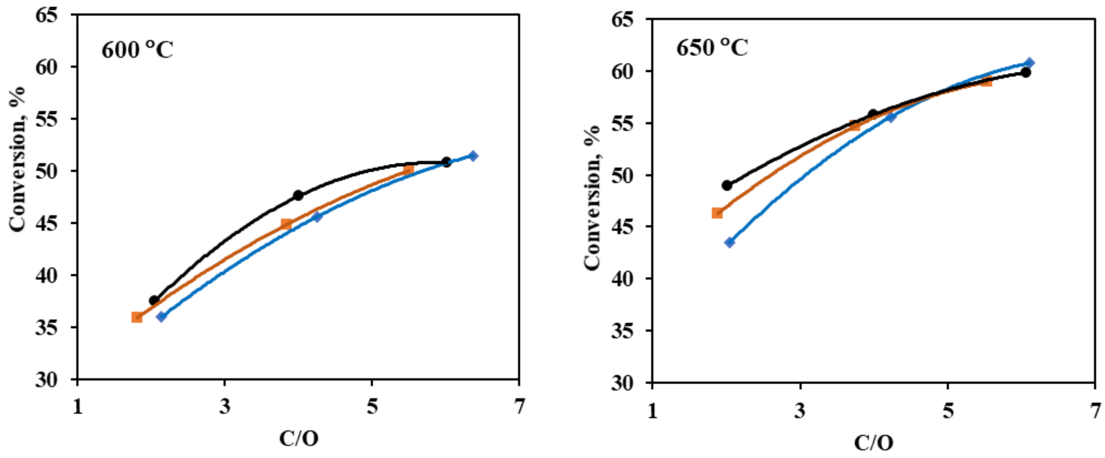

Figure 27 Effect of C/O ratio on conversion for catalytic cracking of (●) AL, (■) AXL, and (♦) ASL crude oils, at 600 ºC and 650 ºC.

As shown in Figure 27 the conversion for all crude oils was plotted versus the C/O ratio. Generally, for the three crudes the increase in C/O ratio led to increase in the conversion. In the C/O ratio range 2 to 4 the relationship between C/O ratio and conversion was linear. The further increase in C/O ratio showed a slight increment in conversion. This performance is a typical one for catalytic cracking via the MAT unit that is described by higher impact on the conversion at less severe condition [40]. Difference in conversion for all crude oils at the same C/O ratio and temperature was not that significant. For example, at 600 ºC and C/O ratio of 4 the conversion for AL, AXL, and ASL crude oils was 47.6, 44.9, and 45.6 wt.%, respectively. In addition, the temperature is a major contributor to the conversion. For example, the conversion of AXL crude oil was enhanced form 35.8 wt.% at 600 ºC up to 46.3 wt.% at the same C/O ratio of 2 as presented in Tables 17 and 18. The uppermost conversions were 59.9, 58.9, and 60.8 wt.% for AL, AXL, and ASL, respectively, achieved at 650 ºC over a C/O ratio of 6.

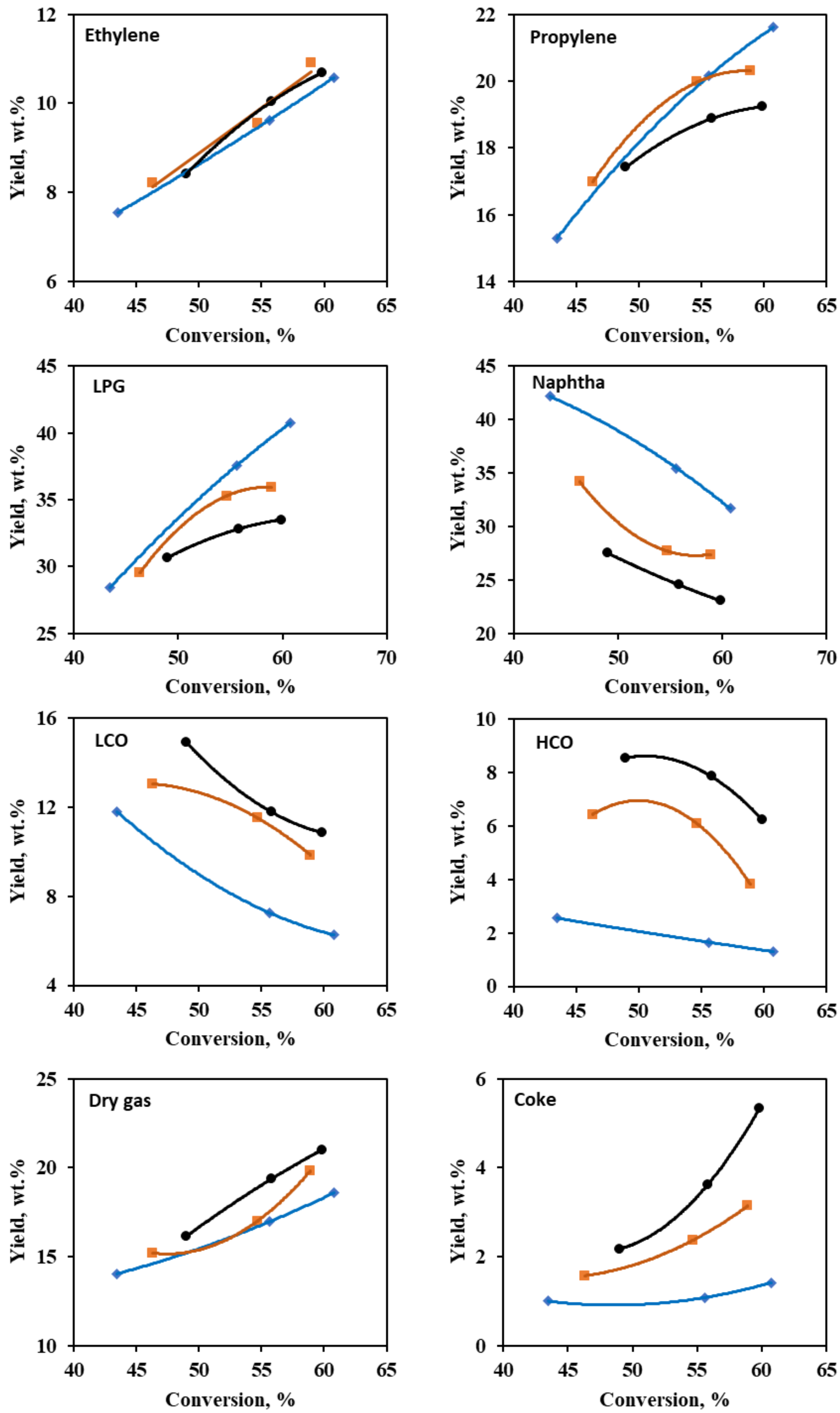

Figure 28 Effect of conversion on product yields for catalytic cracking of (●) AL, (■) AXL, and (♦) ASL crude oils at 650 ºC.

5.4.1 LPG and Light Olefins Yields

In general, as conversion increased yield of LPG increased for all crude oils, at both temperatures 600 and 650 ºC. At 600 ºC in the whole range of conversion, LPG yield for all crudes was nearly the same, as shown in Table 17. For example, the LPG yield at 600 ºC at C/O ratio of 2 for AL, AXL, and ASL was 29.6, 26.5, and 27.8 wt.% respectively. At 650 ºC, there was much variation in LPG yield between the three crudes. The LPG yield at 650 ºC and C/O ratio of 6 increased in order: AL (33.5 wt.%) < AXL (35.9 wt.%) < and ASL (40.8 wt.%). The increase in LPG is accredited to the hydrogen transfer coefficient. HTC is a bimolecular reaction which necessitates compounds to be in a close proximity to strong acidic sites [48]. Naphthenes and olefins that are formed via the primary reactions from the hydrocarbons are consumed by hydrogen transfer reactions to produce aromatics and paraffins [22]. From Tables 17 and 18, The increase in C/O ratio at the same temperature led to increase the HTC. However, the increase in temperature at the same C/O ratio decreased the HTC. ASL crude oil showed the highest HTC for all experiments. Furthermore, the effect of conversion on LPG olefinicity is illustrated in Figure 28. For all crude oils, the LPG olefinicity decreased by increasing the conversion. ASL crude oil showed the lowest LPG olefinicity of 2.0 at C/O ratio of 6 and temperature of 600 ºC (Table 17). At higher temperature (650 ºC) the same behavior was observed, however, the LPG olefinicity was higher. For example, at C/O ratio of 6 the LPG olefinicity of AXL crude oil at 600 and 650 ºC was 2.7, and 5.1, respectively. The increase in LPG olefinicity is ascribed to the selectivity of catalytic cracking to produce higher yields of olefins compared to paraffins at high C/O ratios.

Table 17 Catalyst to oil (C/O) ratio effect on product yields for ASL, AXL, and AL crude oils catalytic cracking at 600 °C, over M-cat/E-cat.

Feed	**ASL**			**AXL**			**AL**		
Mass balance	95.3	95.3	95.6	91.7	94.6	93.8	93.8	93.3	96.6
C/O	2.15	4.25	6.37	1.81	3.84	5.50	2.05	4.01	6.01
Conversion (%)	36.0	45.6	51.5	35.8	44.9	50.0	37.5	47.6	50.8
Yields (wt.%)									
H_2	0.1	0.1	0.2	0.1	0.1	0.2	0.1	0.2	0.2
C_1	1.5	1.7	1.8	1.7	1.8	2.1	2.0	2.3	2.3
C_2	1.4	1.7	1.9	1.6	1.8	2.1	1.8	2.2	2.3
$C_2^=$	**4.6**	**6.1**	**7.0**	**4.9**	**6.1**	**7.3**	**5.0**	**6.6**	**7.2**
C_3	2.0	3.7	5.4	1.9	3.8	4.9	2.0	3.7	5.0
$C_3^=$	**12.8**	**15.4**	**16.5**	**13.2**	**15.5**	**16.6**	**13.4**	**16.4**	**16.8**
iC_4	1.9	3.3	4.4	1.0	2.3	3.0	0.9	2.0	2.6
nC_4	2.2	2.8	3.3	1.0	1.6	2.0	1.4	1.9	2.2
Total Gas	35.5	44.8	50.3	34.9	43.2	47.6	35.9	45.2	47.7
Naphtha	**49.4**	**44.2**	**41.3**	**37.3**	**34.8**	**33.2**	**31.4**	**29.3**	**28.3**
LCO	11.9	8.6	6.0	17.6	13.2	12.2	16.7	14.1	13.1
HCO	2.7	1.6	1.2	9.2	7.1	4.6	14.3	9.0	7.8
Coke	0.5	0.8	1.2	1.0	1.6	2.4	1.6	2.4	3.2
$C_2^=$ + $C_3^=$	**17.5**	**21.6**	**23.5**	**18.1**	**21.6**	**23.9**	**18.4**	**23.0**	**23.9**
H_2-C_2 (dry gas)	7.6	9.6	10.9	8.3	9.9	11.6	8.9	11.2	12.0
C_3-C_4 (LPG)	27.8	35.1	39.5	26.5	33.4	36.0	26.9	34.0	35.7
$C_2^=$-$C_4^=$	**26.5**	**31.6**	**33.5**	**27.5**	**31.6**	**33.5**	**27.6**	**33.0**	**33.1**
$C_4^=$	9.0	10.0	9.9	9.4	10.1	9.7	9.2	10.0	9.1
HTC	0.4	0.6	0.8	0.2	0.4	0.5	0.2	0.4	0.5
CMR	4.1	3.0	2.5	8.2	4.2	3.9	9.8	5.8	4.7

P/E	2.8	2.5	2.3	2.7	2.5	2.3	2.7	2.5	2.3
C_1-C_4	8.9	13.1	16.7	7.2	11.5	13.9	8.1	12.0	14.4
LPG olefins	21.8	25.4	26.4	22.6	25.6	26.2	22.6	26.4	25.9
LPG paraffins	6.0	9.7	13.0	3.9	7.8	9.8	4.3	7.6	9.8
LPG olefinicity	3.6	2.6	2.0	5.8	3.3	2.7	5.3	3.5	2.6
Ratios (mol/mol)									
$C_2^{=}/C_2$	3.4	3.9	4.1	3.2	3.6	3.8	2.9	3.3	3.4
$C_3^{=}/C_3$	6.9	4.4	3.2	7.2	4.2	3.6	6.9	4.6	3.5
$C_4^{=}/C_4$	2.3	1.7	1.3	5.0	2.6	2.0	4.2	2.7	2.0
$iC_4^{=}/C_4^{=}$	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
$iC_4^{=}/iC_4$	1.8	1.1	0.8	3.5	1.6	1.2	3.8	1.9	1.3

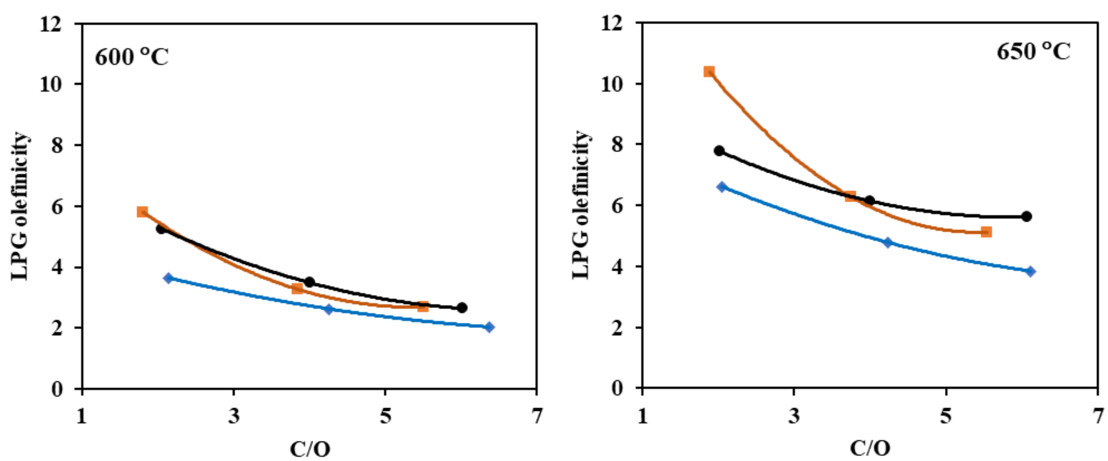

Figure 29 Effect of conversion on LPG olefinicity for catalytic cracking of (●) AL, (■) AXL, and (♦) ASL crude oils, at 600 ºC and 650 ºC.

Yields of ethylene versus conversion were plotted in Figure 28 at 650 ºC. For all crude oils, the yield of ethylene increased by increasing both C/O ratio and temperature. To a lower extent, AL crude oil produced more ethylene than other crude oils. On the other hand, ASL crude oil yielded a lower amount of ethylene. For example, as shown in Table 17 the yields of ethylene at 600 ºC at a C/O of 4 for AL, AXL, and ASL crude oils were 6.6, 6.1 6.1 wt.%, respectively. Due to high severity and more cracking, the yield of ethylene exhibited an increase at high temperature. For instance, the yield of ethylene from AL crude oil cracking was enhanced from 7.2 wt.% at 600 ºC up to 10.7 wt.%.

Figure 28 shows the conversion effect on propylene yield. As expected, the conversion had a positive effect on the yield of propylene. At 600 ºC for the whole range of conversion, the yield of propylene decreased in order, AL, AXL, and ASL crude oils. For example, the yield of propylene at highest conversion was 16.8 wt.% for AL, 16.5 wt.% for AXL, and 16.5 wt.% for ASL crude oil. In contrast, at 650 ºC the order reversed. ASL crude oil at C/O ratio of 6 resulted in the largest yield of propylene of 21.6 wt.% while AL crude oil produced the lowest yield of 19.2 wt.%.

The ratio of P/E for the three crude oils followed the same trend. At 600 ºC for all crude oils, the P/E ratio at C/O ratio of 2, 4, 6 was: 2.7, 2.5, and 2.3, (Table 17) respectively. At 650 ºC for all crude oils and at all C/O ratios the P/E ratio was nearly constant with a value of 2.0 ±0.1. Furthermore, the ratio of C_2=/C_2 for all crude oils increased with increasing C/O ratio. For example, for ASL crude oil the C_2=/C_2 ratio at 600 ºC at C/O ratio of 2, 4, and 6 was: 3.4, 3.9, and 4.1, respectively. In addition, the values of C_2=/C_2 at the same C/O ratio decreased in order: ASL, AXL, and AL. On other hand, the C3=/C3 ratio declined by increasing the C/O ratio. For instance, at 650 ºC the of C_3=/C_3 ratio decreased from 12.3 at C/O ratio of 2 down to 5.9 at C/O ratio of 6.

5.4.2 Naphtha, LCO and HCO Yields

Naphtha is produced by the cracking of LCO and HCO, at the same time, naphtha is cracked to produce light products mainly light olefins [23]. Generally, the yield of naphtha decreased by the increase in C/O ratio (conversion) and temperature. For, example, the yields of naphtha for ASL crude oil at 600 ºC at C/O ratios of 2, 4, and 6 were, 49.4, 44.2, and 41.3 wt.% respectively. The increase in temperature from 600 to 650 ºC decreased the yield of naphtha of AXL from 34.8 to 27.7 wt.% (Tables 17 and 18). At both temperatures 600 and 650 ºC the order of yield of naphtha increased in order: AL, AXL, and AL crude oil. For example, the yield of naphtha at 600 ºC at C/O ratio of 6 for AL, AXL, and ASL crude oils were, 28.3, 33.2, and 41.3 wt.%, respectively. The decrease in naphtha yield is associated with an enhancement in the yield of light olefins.

Yields of LCO and HCO are plotted versus conversion in Figure 28 for the three crude oils at 650 ºC. As shown in Tables 17 and 18, as the C/O ratio was increased, yields of LCO and HCO decreased due to further cracking. For example, for the cracking of AXL at 600 ºC as the C/O ratio increased from 2 to 6 the yields of LCO and HCO decreased from 17.6 and 9.2 wt.% to 12.2 and 4.6 wt.%, respectively. In addition, the temperature plays an important role in cracking the heavy cuts (LCO and HCO). For instance, from Tables 17 and 18 for the cracking of AXL crude oil at C/O ratio of 4, by the increment of temperature from 600 to 650 ºC the yields of LCO and HCO decreased from 13.2 and 7.1 wt.% down to 11.5 and 6.1 wt.%, respectively. At the same condition, C/O ratio and temperature, the yields of LCO and HCO decreased in order: AL < AXL < ASL. For example, at 650 ºC and C/O ratio of 6 the yields of HCO and LCO for AL were 6.2 and 10.9 wt.%, for AXL were 3.8 and 9.9 wt.%, and for ASL were 1.3 and 6.3 wt.%, respectively. Figure 30 presents products distribution versus feed composition for catalytic cracking of the AL, AXL, and ASL crude oils at 650 ºC and C/O ratio of 6. The differences in yields of naphtha, HCO, and LCO between the three crude oils are attributed to the initial amount of these fractions in the feeds.

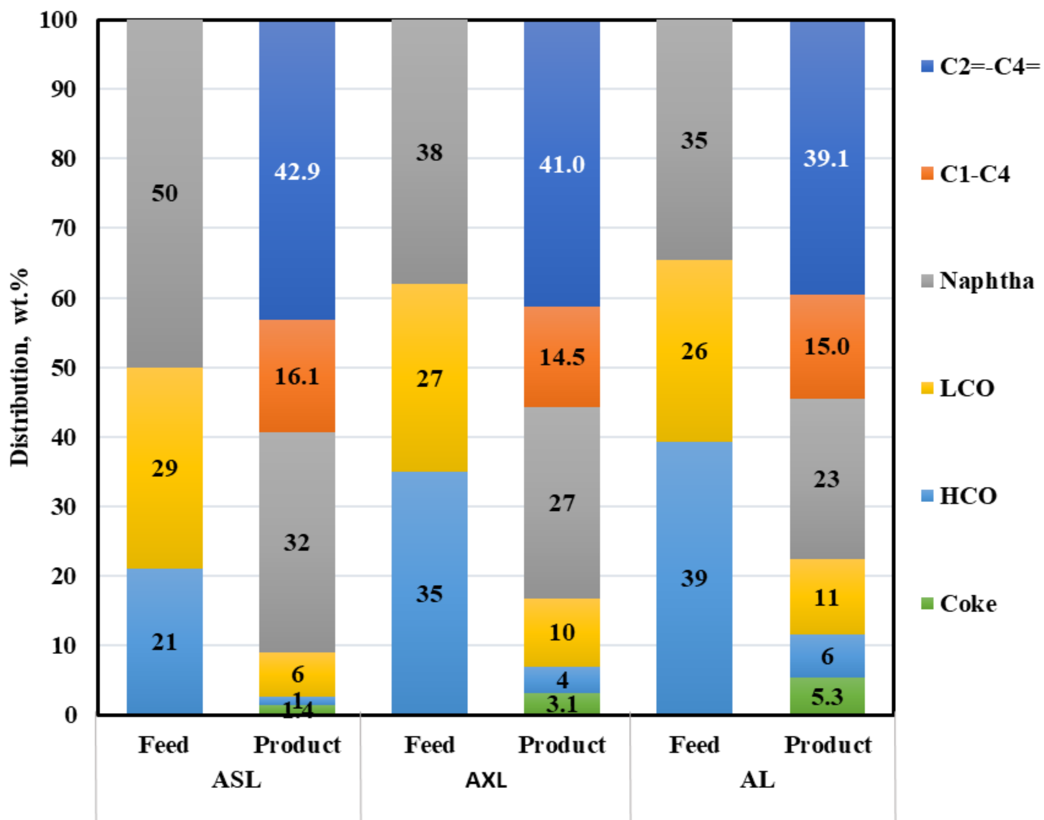

Figure 30 Products yield distribution for catalytic cracking of AL, AXL, and ASL crude oils compared to feeds, C/O of 6 and at 650 ºC.

5.4.3 Dry Gas and Coke Yields

Yields of dry gas for the three crude oils were plotted conversion at 650 ºC (Figure 28). ASL crude oil yielded the lowest dry gas followed by AXL and then AL crude oil. For example, from Table 17 the yields of dry gas at 600 ºC and C/O ratio of 4 for ASL, AXL, and AL were 9.6, 9.9, and 11.2 wt.%, respectively. Moreover, the increase in the C/O ratio improved the dry gas yield for all crude oils. For instance, the dry gas yields for AXL crude oil at 650 ºC and C/O ratios of 2, 4, and 6 were 15.2, 17.0, and 19.8 wt.%, respectively. Furthermore, the rise in temperature further boosted the yield of dry gas. An example of the temperature effect is the increase in dry gas yield of the cracking of ASL crude at C/O ratio of 2 from 7.6 wt.% at 600 ºC up-to 14.0 wt.% at 650 ºC. The main reason of the increment in the yield of dry gas is the further enhancement in ethylene yield.

The CMR values are shown in Tables 17 and 18 at 600 and 650 ºC, in order to compare the variations in yield of dry gas. AL crude oil showed the highest CMR at all conditions followed by AXL and then ASL. The rise in reaction temperature showed an increase in CMR due to the influence of protolytic cracking compared to beta-session and carbenium ion mechanisms [22]. For example, for the ASL crude oil cracking at C/O ratio of 2, the CMR increased from 4.1 at 600 ºC up-to 18.0 at 650 ºC. In addition, the increase in the C/O ratio caused a reduction in the CMR, which is caused by the further enhancement in the yield of isobutane more than the increase in the yield of dry gas. An illustration of the C/O ratio effect on the CMR is the reduction in CMR of AXL crude oil at 650 ºC from 33.1 at C/O ratio of 2 down to 15.8 at C/O ratio of 6 (Table 18).

Table 18 Catalyst to oil (C/O) ratio effect on product yields for ASL, AXL, and AL crude oils catalytic cracking at 650 ºC, over M-cat/E-cat.

Feed	**ASL**			**AXL**			**AL**		
Mass balance	96.6	96.1	96.1	93.9	94.9	92.7	91.2	93.7	92.3
C/O	2.04	4.24	6.12	1.88	3.75	5.54	2.02	4.00	6.07
Conversion (%)	43.5	55.6	60.8	46.3	54.7	58.9	49.0	55.8	59.9
Yields (wt.%)									
H_2	0.2	0.3	0.3	0.2	0.2	0.3	0.2	0.3	0.3
C_1	3.7	4.1	4.4	3.9	4.0	4.8	4.3	5.1	5.7
C_2	2.6	3.0	3.3	2.9	3.2	3.8	3.2	3.9	4.3

$C_2^=$	**7.5**	**9.6**	**10.6**	**8.2**	**9.6**	**10.9**	**8.4**	**10.0**	**10.7**
C_3	1.3	2.7	3.8	1.5	2.8	3.4	1.9	2.7	2.9
$C_3^=$	**15.3**	**20.2**	**21.6**	**17.0**	**20.0**	**20.3**	**17.4**	**18.9**	**19.2**
iC_4	0.8	1.7	2.3	0.5	1.0	1.3	0.5	0.7	0.9
nC_4	1.6	2.1	2.3	0.6	1.0	1.2	1.1	1.2	1.3
Total Gas	42.5	54.5	59.3	44.7	52.3	55.8	46.8	52.2	54.5
Naphtha	**42.2**	**35.5**	**31.7**	**34.2**	**27.7**	**27.4**	**27.5**	**24.5**	**23.0**
LCO	11.8	7.3	6.3	13.0	11.5	9.9	14.9	11.8	10.9
HCO	2.6	1.7	1.3	6.4	6.1	3.8	8.6	7.9	6.2
Coke	1.0	1.1	1.4	1.6	2.4	3.1	2.2	3.6	5.3
$C_2^=$ + $C_3^=$	**22.8**	**29.8**	**32.2**	**25.2**	**29.5**	**31.2**	**25.8**	**28.9**	**29.9**
H_2-C_2 (dry gas)	14.0	17.0	18.6	15.2	17.0	19.8	16.1	19.4	21.0
C_3-C_4 (LPG)	28.4	37.6	40.8	29.5	35.3	35.9	30.7	32.8	33.5
$C_2^=$-$C_4^=$	**32.2**	**40.7**	**42.9**	**35.1**	**40.0**	**41.0**	**35.6**	**38.3**	**39.1**
$C_4^=$	9.4	10.9	10.7	9.9	10.5	9.8	9.8	9.4	9.2
HTC	0.3	0.3	0.4	0.1	0.2	0.2	0.2	0.2	0.2
CMR	18.0	9.7	8.1	33.1	16.8	15.8	30.4	26.0	22.3
P/E	2.0	2.1	2.0	2.1	2.1	1.9	2.1	1.9	1.8
C_1-C_4	10.0	13.5	16.1	9.4	12.0	14.5	11.0	13.6	15.0
LPG olefins	24.7	31.1	32.3	26.9	30.5	30.1	27.2	28.2	28.4
LPG paraffins	3.7	6.5	8.4	2.6	4.8	5.9	3.5	4.6	5.1
LPG olefinicity	6.6	4.8	3.8	10.4	6.3	5.1	7.8	6.1	5.6
Ratios (mol/mol)									
$C_2^=/C_2$	3.2	3.5	3.5	3.0	3.2	3.0	2.8	2.8	2.7
$C_3^=/C_3$	12.3	7.9	5.9	11.9	7.5	6.2	9.8	7.4	7.0
$C_4^=/C_4$	4.0	3.0	2.4	9.3	5.3	4.2	6.2	5.0	4.3
$iC_4^=/C_4^=$	0.3	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
$iC_4^=/iC_4$	4.2	2.3	1.7	7.8	3.8	2.8	6.7	4.5	3.5

Figure 28 demonstrates the coke formation versus conversion for AL, AXL, and ASL crude oils at 650 ºC. The amount of coke produced depends on the feed composition, particularly the percentage of heavy cuts, C/O ratio, and temperature. As the feed gets heavier the amount of coke that deposited on the catalyst gets higher. At all conditions, the order of coke yield followed the same order of the density of the crude oils which is in a decreasing order: AL, AXL, and ASL. For example, at a constant C/O ratio of 6 and temperature of 650 ºC the coke yields for AL, AXL, and ASL were 5.3, 3.1, and 1.4 wt.%, respectively. Moreover, the amount of coke produced increases with increasing temperature of the process. For instance, as shown in Tables 17 and 18 the coke yields at 600 and 650 ºC for the AL crude oil cracking were 3.2 and 5.1 wt.%, respectively.

Figure 31 illustrates the differences between thermal and catalytic cracking (C/O ratio of 6) in terms of light olefins and naphtha yields for AL, AXL, and ASL crude oils. Catalytic cracking showed a high selectivity towards producing more light olefins for all crude oils. ASL crude oil showed the largest gap between thermal and catalytic cracking with a yield of 19 wt.% for thermal and 43 wt.% for catalytic cracking. On the other hand, naphtha yield for thermal catalytic was higher than for catalytic cracking. Similarly, ASL crude oil showed the highest difference in naphtha yield between thermal and catalytic cracking with a gap of 16 wt.%. Thermal cracking low yields of naphtha is caused by the cracking of naphtha-range hydrocarbons into light olefins. This reason is evidenced by the higher yield of light olefins.

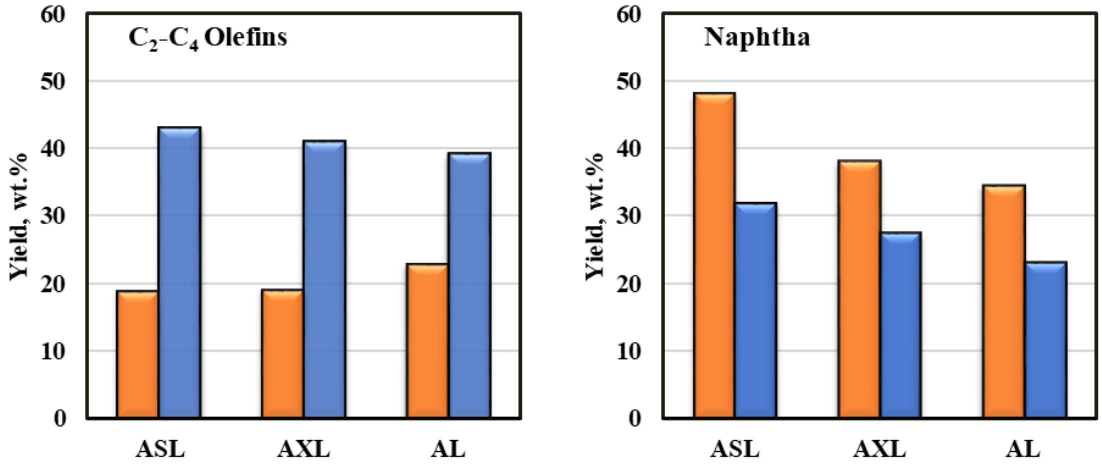

Figure 31 Light olefins and naphtha yields for AL, AXL, and ASL crude oils via (■) thermal and (■) catalytic cracking (C/O of 6) and at 650 ºC.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

6.1 Background

In this chapter all the findings of this work are summarized and recommendations for future work in the field of crude oil cracking are listed.

6.2 Conclusions

Catalytic cracking was conducted by using two catalysts, M-cat (ZSM-5) and E-cat at 550-650 °C. At constant conversion, catalytic cracking showed higher yields of propylene, LPG, and C_4 olefins than thermal cracking. For example, propylene yield was 10.8 wt.% and 8.6 wt.% for M-cat and thermal, respectively. On the other hand, thermal cracking yielded more dry gas (C_1-C_2 and H_2) due to the high amount of ethylene, which shows the effect of high temperature on pyrolytic cracking. At high temperature (650 °C) and catalyst to oil ratio of 4, the olefins yield decreased in order M-cat (32.7 wt.%) > E-cat (30.3 wt.%) > thermal cracking (22.8 wt.%). The highest yields of ethylene and propylene were 10.9 wt.% and 15.7 wt.%, respectively, achieved over M-cat at 650 °C. The higher yield for M-cat over E-cat is explained by shape selectivity and higher acidity. The naphtha yield for E-cat was much higher than M-cat. For instance, at 550 °C it was 48.3 wt.% for E-cat and 24.4 wt.% for M-cat. The effect of C/O ratio on conversion and yields showed that after C/O of 4 the increase in C/O ratio had a minor effect on the conversion and yields except for coke. Finally, mixing E-cat and M-cat boosted the yields of light olefins with an optimum composition of 42% E-cat. The yields of ethylene and propylene at this composition were 10.7 wt.% and 19.2 wt.% respectively.

Catalytic cracking of three light crude oils was conducted by using E-cat, M-cat, and a mixture of 30% M-cat and E-Cat at 600-650 °C. For thermal cracking, for all crude oils as the temperature increased conversion and yields of light olefins, LPG, dry gas and coke increased, associated with decrease in yields of naphtha, LCO, and HCO. For thermal cracking at 650 °C, the yields of corresponding ethylene and propylene increased in order: ASL (6.1 and 6.8 wt.%) < AXL (6.5 and 6.9 wt.%) < AL (7.6 and 8.6 wt.%) crude oils. In addition, the yields of naphtha at 650 °C for ASL, AXL, and AL were 48.0, 38.1, 34.4 wt.%, respectively. The large differences in naphtha, LCO, and HCO yields are attributed to the initial naphtha content in the crude. The total yield of ethylene and propylene increased in order: AL (25.8 wt.%) < ASL (26.3 wt.%) < AXL (27.4 wt.%), over M-cat/E-cat. The yields of naphtha followed the same behavior as thermal cracking. Furthermore, the effect of catalyst to oil (C/O) ratio over M-cat/E-cat for all the crude oils was inspected at two temperatures (600 and 650 °C). The effect of C/O ratio on conversion of the three crude oils, was also examined, and showed that after C/O of 4 the further increases in C/O ratio resulted only in a minor effect. Moreover, the increase in C/O ratio and temperature enhanced yields of ethylene, propylene, butenes, LPG, dry gas, and coke associated with a consistent decrease in middle and heavy ends (naphtha, LCO, and HCO). The highest yield of ethylene and propylene for AL, AXL, and ASL were 29.9, 31.2, and 32.2 wt.% respectively, were achieved at 650 °C and a C/O ratio of 6.

6.3 Recommendations

Crude oil cracking is considered to be a relatively new research area, so lots of improvements can be implied.

First of all, feed pre-treatment can be investigated, such as hydrodesulfurization and de-metallization. In addition, the metals, that are present in the feed, effect of the catalysts can be studied. In addition, kinetic modeling of thermal and catalytic cracking shall be implied.

Furthermore, the Advanced Cracking Evaluation (ACE) unit and the pilot plant shall be used for further studies for the cracking o crude oil to investigate the effect of fluidization and cracking of much larger amounts of feed.

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Submitted patents	Suliman Al-Khattaf, Akram Al-Absi and Abdullah Aitani. Integrated Process for Catalytic Cracking of whole Crude Oil to Light Olefins. Suliman Al-Khattaf and Akram Al-Absi. Catalytic Conversion of Whole Arab Super Light and Arab Extra Light Crude Oils in High Temperature FCC Process into Light Olefins and Gasoline.